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# The Impact of Oily Materials on Activated Sludge Systems

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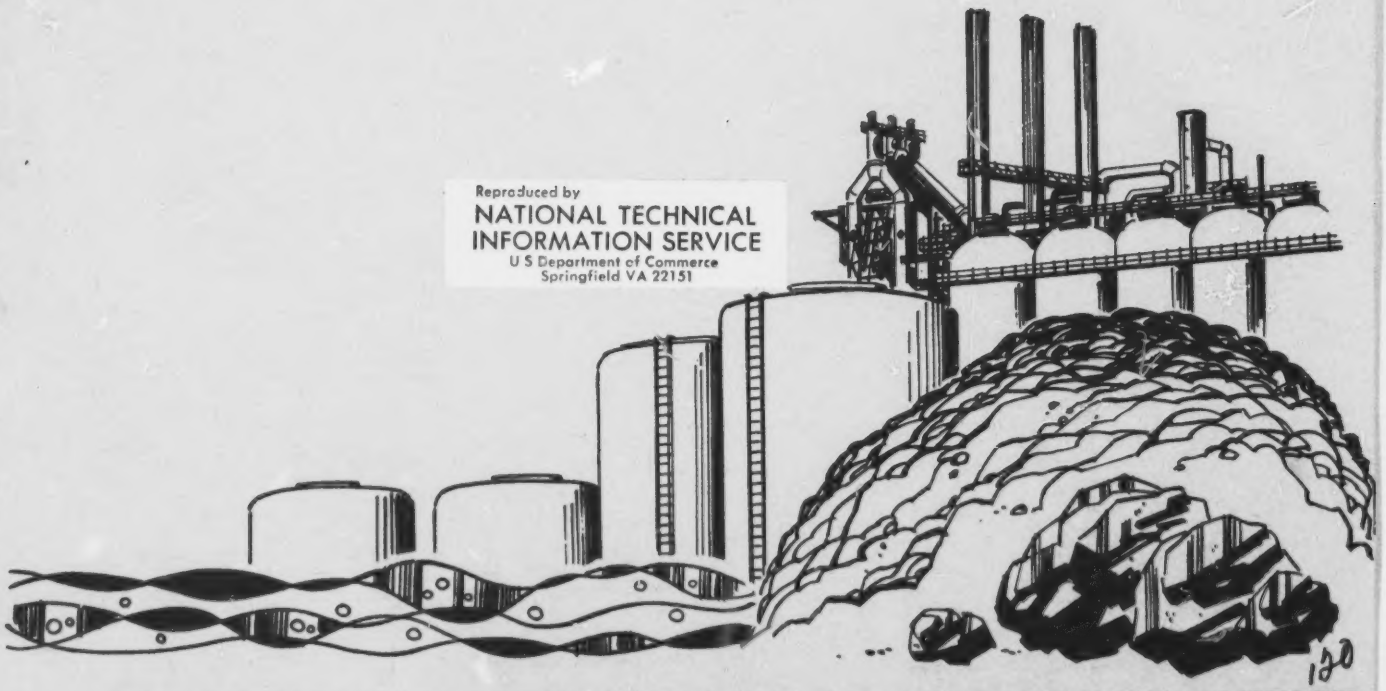

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The performance of small scale continuous activated sludge systems was observed after being exposed to a variety of oily compounds such as crankcase oil, crude oil and vegetable oil, at several loading levels. Batch studies were conducted to determine biodegradability and the effect of emulsification and temperature on the rate of biological reaction. Oils are absorbed on the floc and slowly degrade when they are introduced into an activated sludge system. The oil accumulates on the sludge causing a loss of density and acceptable settling characteristics if the loading rate is higher than the degradation wastage. The ability of the microbial system to remove other substrates is not inhibited although the biological system fails due to the loss of sludge. 0.10 pounds per day per pound of sludge under aeration should be the maximum continuous feed level of oils to activated sludge. Shock loads should not exceed 5% of the weight of the sludge under aeration. (Smith-Texas)

*Oil wastes, *Activated sludge, *Sewage treatment, *Waste water disposal, Biological treatment, Oil, Biodegradation, Absorption, Sludge treatment

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# THE IMPACT OF OILY MATERIALS ON ACTIVATED SLUDGE SYSTEMS

Submitted to:

The American Petroleum Institute
Committee for Air and Water Conservation

and

Industrial Pollution Control Branch
Environmental Protection Administration

by:

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07675

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March 1971

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## ABSTRACT

Small scale continuous activated sludge systems were exposed to a variety of oily compounds at several loading levels and performance observed. Batch studies to determine biodegradability and the effect of emulsification and temperature on the rate of biological reaction were also conducted.

Oils introduced into an activated sludge system are absorbed on the floc and slowly degrade. If the loading rate is higher than the degradation rate and the rate of wastage, the oil accumulates on the sludge. This accumulation causes a loss of density and a loss of acceptable settling characteristics. The biological system fails due to the loss of sludge but the ability of the microbial system to remove other substrates is not inhibited.

The continuous feed level of oils to activated sludge should not exceed 0.10 pounds per day per pound of sludge under aeration. Shock loads should not exceed 5% of the weight of the sludge under aeration.

The study also considered physical separation of oils before biological treatment, and various chemical methods of separating complex emulsions.

This report is submitted in fulfillment of Grant Project No. 12050DSH between the Environmental Protection Agency and the American Petroleum Institute.

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## CONCLUSIONS AND RECOMMENDATIONS

1. Oily materials introduced into an activated sludge system are almost immediately absorbed on the biological floc. (Page 57)

2. Excessive amounts of oily materials interfere with the performance of an activated sludge system by lowering the density of the floc to the level where the sludge settling properties are destroyed. (Pages 55-57)

3. Within the concentration limits explored in this study, oily material in a system does not interfere with the ability of the microbes to efficiently oxidize other substrates in the system.

4. Soluble hydrocarbons do not appear to interfere with activated sludge treatment. (Pages 27-29)

5. An activated sludge system will perform satisfactorily with a continuous loading of hexane extractables of 0.1 pounds per pound mixed liquor suspended solids. Questionable stability develops at a loading of 0.15 pounds HE per pound mixed liquor suspended solids. For conventional plant operations, the influent to the biological system should contain less than 75 mg/l hexane extractable materials and preferably less than 50 mg/l.

6. The impact of a particular shock load of oily material on an activated sludge may be estimated by calculating the resulting density of the system. In general, a load equivalent to 5% of the sludge weight under aeration is acceptable, while a 10% load will cause significant upset in the system. (Pages 49-54)

7. Each of the oily materials studied could be biologically degraded to some degree. The oxidation rate as compared to a sewage-like substrate was very slow and even after extensive contact, a significant residue of oily substrate remained. (Pages 25-26)

8. Increasing the solids under aeration will improve the ability of an activated sludge system to withstand a high loading of oily compounds but wherever possible, the level of hexane soluble material entering such systems should be minimized. (Pages 73-74)

9. This study has shown that in most cases, all necessary oil separation can be achieved by simple aeration followed by gravity separation. These features can be incorporated in the

grit chamber-settling tank designs of most plants.

10. For highly emulsified systems pretreatment by air flotation, with chemical addition in some cases, provided a satisfactory primary effluent for activated sludge feed.

## RECOMMENDATIONS FOR FURTHER STUDY

1. An engineering study of the modification required to maximize oil removal in an aerated grit chamber-settling tank combination should be considered.

2. In view of the problems encountered in the analytical measurements and systems operations aspects of this project, considerable efforts to develop better methodology should be the starting point of any further study of this phenomena.

3. The fate of an oil laden floc escaping to the receiving stream should be investigated.

4. Methods of preventing solids loss should be investigated. Final filtration appears to be the most promising method in this regard.

5. The impact of oil materials on the sludge handling portion of the plant should be studied.

# INTRODUCTION

This project was undertaken to investigate the capability of biological systems to assimilate various oils. It has been reported that when an activated sludge system becomes overloaded with oily materials, a deterioration in treatment occurs. The conditions under which such adverse behavior occur are poorly defined. As a result of real or anticipated problems, most municipalities have enacted strict ordinances controlling the discharge of oils and greases. Typical ordinances call for the total elimination of any free and/or floating oils, while the concentration of hexane soluble materials in the flow is usually restricted to 50 mg/l or less. There is little information available upon which to base an evaluation of the validity and necessity of such restrictions. Furthermore, there is little information available on how a treatment plant will be affected by a loading of oily materials, or how to operate such a facility to minimize the inherent problems.

The manner in which oily materials cause system failure is of considerable concern. The system failure can be either biochemical or physical; that is, the inhibition may occur either within the microbial population itself, or in the environment necessary for its performance and life. If oils are removed by a biological system, the mechanism by which the removal is accomplished must be defined to understand the reactions of the biological system. Definition of the nature of any interference is essential. The effect of oil loadings on oxygen transfer ability and the adsorptive ability of the sludge must be considered. In addition, studies must be conducted to evaluate sludge coagulation and settling to determine if system deterioration occurs in these areas. Once the nature of the interference is understood, techniques can be developed to overcome the problem to the greatest possible extent. Also, improved methods of pretreatment are considered essential in that a more efficient removal of the oily materials before they enter secondary treatment will aid in preserving the treatment efficiency of the system.

## Project Objectives

The present study was undertaken in an attempt to generate useful data on the operation and improvement of biological systems subject to continuous or intermittent discharges of a variety of oily materials. The project objectives were:

1. To determine the tolerance of municipal and industrial waste treatment systems to various oily materials.

2. To determine the nature of the interference of oily materials with biological treatment.

3. To determine the fate of oil materials in biological systems above and below the tolerance limits of the systems.

4. To study methods of operation which would improve the ability of biological systems to assimilate oils.

5. To examine methods of improving pretreatment of oily materials in municipal and industrial waste systems.

## PLAN OF OPERATION

Four oily materials, spent crankcase oil, vegetable oil, refinery waste oil, and crude oil were chosen as the primary test substrates. Spent crankcase oil and vegetable oil find their way to most sewage treatment plants as the result of a variety of municipal operations, while waste oil or crude oil would only reach a municipal plant as the result of an industrial accident or system failure. Some effort was directed toward identifying any potential treatment plant problems associated with benzene or its derivatives.

The main course of the study involved the operation of small scale activated sludge units at conditions similar to normal domestic plants and measuring and observing the impact of various concentrations of the test substrates on this performance. In addition to such studies, a variety of batch and semi-continuous systems studies were conducted to develop supporting information.

It became obvious through the biological studies that sieable slugs of oily materials should be precluded from entering biological treatment. The second phase of the study concerned itself with the possible pretreatment method for oil removal. Both physical and chemical methods of agglomeration and separation were conducted.

### Reports by Others

The literature concerning the fate of hydrocarbons in biological systems is sketchy, and in some cases, contradictory. Certainly a good part of the confusion results from the difficulty in measuring the presence and persistence of the hydrocarbons by the tests conventionally employed in sanitary engineering studies. Although such investigators as Ludzack, et.al.,[18,19] have observed degradation of hydrocarbons ranging from between 50 and 80 percent in aerobic systems, it is questionable whether the investigator observed complete oxidation of mateirals, or only a partial oxidation of the study substrates. Benger[7] reports that a large percent of the observed change does not result in ultimate degradation of materials but simply in modification. In all cases, it is apparent however, that complete degradation of materials is not obtained in conventional systems.

"Oil wastes which escape treatment enter the stream primarily as emulsified materials. The oil globules are then trapped in the flocculent biological solids, conglomerate and settle. The sedimentation results in the formation of partially decomposed beds beneath the water surfaces. As warm weather occurs

and the beds become anaerobic, gasification of the sludge tends to lift the oil and solids back into the flowing water. This action results in a general lowering of water quality and in some cases, in the collection of these materials at shoreline.[19]

The principal concern with the collection of significant information on the fate of hydrocarbons is the lack of suitable methodologies to determine the concentration and type of hydrocarbons present either in the waste or in the sludge. Conventional BOD and COD techniques have been employed by several investigators. The results obtained have been at best, partially indicative of the concentration of materials; at worst, the materials have shown little response to the BOD or COD tests. Techniques such as adsorption on an activated carbon with subsequent extraction or collection on inorganic solids have proved more successful, but have limited applications in cases concerned with activated sludge. Spectrophotometric techniques have been used successfully in some cases.

Studies by McKinney[20] have shown that specific oily substrates will undergo oxidation to a rather high degree, if the proper conditions are maintained. These conditions are however, significantly different from those normally encountered in a municipal sewage treatment plant.

Anaerobic treatment has been applied in various studies, with little or no degradation of hydrocarbons being observed. Investigators disagree on the nature and extent of interferences caused with anaerobic digestion. Here again, it is probable that partial degradation of the materials occurs; whether or not significant reduction in overall hydrocarbon concentration is obtained is highly questionable.

There is significant evidence that emulsions holding the oil within the waste are broken during biological treatment. Experience by several investigators has shown that the inclusion of secondary skimming devices in industrial plants can be of major aid in controlling the discharge of oils to the receiving stream. It has also been found that oils and similar materials accumulate in the biological sludges that are returned to the aeration tanks. Most investigators report difficulty in obtaining accurate measurements of oily materials bound with the sludge. This is principally due to the difficulty in separating the oils from the sludge floc. Special sampling techniques are required if proper, proportional, samples are to be obtained.

A large amount of information is available concerning physical and chemical treatment for the removal of oils. By far, the most popular method employed today is the use of an API separator; design criteria for these units have been widely published.

The units are, in general, quite effective and succeed in removing floating oil with the efficiency dependent on the type of material enccuntered.

Use of cnemicals to break oil emulsions is widespread. Significant information on the efficiency of alum and lime in aiding such processes, the use of polyelectrolytes, absorbent clays, demulsifiers, etc., is available in the industrial journals. Air flotation is used in many cases to achieve higher efficiencies. In this type of treatment, difficulties are continually encountered in obtaining proper measurements of the efficiency of the treatment, due to the nature of the material being tested.

In summary then, the literature presents significant information on the physical and chemical treatment of oily materials, but little data is available on the ultimate fate of such materials in biological systems. There are indications, however, that aerobic treatment may be successfully employed to at least partially degrade these materials.

## BIOLOGICAL TREATMENT STUDIES

### Overall Study Discussion

The majority of the biological experiments involved the study of continuous, laboratory scale treatment systems simulating conventional activated sludge treatment plants. Normal systems analysis was supplemented with off stream analyses, such as oxygen utilization rate measurements, settling studies, and respirometer investigations.

After an initial study of the test compounds and the applicability of methods of analyses, a group of experiments were conducted to determine the nature of the reaction between oily materials and activated sludge. The resulting data were supplemented with information describing the biodegradability of the study compounds and the effects of temperature and emulsification on system performance.

Having derived from the first phase of the studies an understanding of how systems will behave, detailed investigations to analyze the influence of oil loading rate, detention time, acclimatization, and waste composition were conducted under varying system conditions.

The final set of experiments considered the behavior of the systems under shock loading conditions and the comparison of performance of an industrial waste treatment system to domestic performance. The study also considered the possible development of a culture that would treat the oily materials alone.

## EXPERIMENTAL STUDIES

### Characteristics Of Test Compounds

The froup of test compounds ıncluded a crude oil, a spent crank case oil, a refinery waste oil, and a vegetable oil. These oil compounds were chosen because they are relatively insoluble materials that are considered to be extremely difficult to remove in biological systems, and are suspected of causing adverse effects on treatment plant performance. In addition, certain benzene derivative compounds were investigated on a preliminary basis. These materials were selected since they are found in the raw waste streams entering treatment facilities.

Initially, these test materials were examined for their physical and biochemical characteristics. The analyses included chemical oxygen demand, biochemical oxygen demand, solvent extractability, total oxygen demand, density, and viscosity.

The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were carried out employing the methods described in "Standard Methods for the Examination of Water and Wastewater" -- 12th Edition. The total oxygen demand associated with the test materials was measured employing respirometer system studies and involved monitoring, for at least one month, the oxygen utilization of a known weight of oily materials. A detailed description of this study is presented in a subsequent section of the report. The density of the oily material was determined by weighing out a known volume of material at a given temperature. A Cannon-Fenske viscometer was used to determine the viscosity of the oils. Table 1 summarizes the results from these analyses.

TABLE 1

CHARACTERISTICS OF TEST SUBSTRATES

| Test Materials | $BOD_5$[1] | COD[2] | Total[3] Oxygen Demand | Percent Hexane Soluble (4) | (5) | Viscosity (centistokes) | Density (gms/ml) |
|---|---|---|---|---|---|---|---|
| Synthetic Sewage | .58 | 0.70 | 0.72 | | | | |
| Crank case oil | .39 | 1.98 | 1.16 | 82 | 88 | 102.6 | 0.899 |
| Crude Oil | .45 | 2.62 | 1.03 | 71 | 83 | 27.6 | 0.846 |
| Refinery Waste | .27 | 0.98 | 1.21 | 50 | 61 | 5.0 | 0.840 |
| Vegetable oil | .48 | 2.37 | 2.05 | 89 | 96 | 76.0 | 0.909 |
| Benzene | .60 | (6) | 1.77 | | | | |

TABLE 1
(continued)

| Test Materials | $BOD_5$[1] | COD[2] | Total[3] Oxygen Demand | Percent Hexane Soluble (4) (5) | Viscosity (centistokes) | Density (gms/ml) |
|---|---|---|---|---|---|---|
| Toluene | 1.00 | 1.40 | 1.80 | | | |
| Toluene | 1.00 | 1.40 | 1.80 | | | |
| Benzoic Acid | 1.38 | 1.96 | 1.67 | | | |
| Benzaldehyde | 2.45 | 1.45 | 2.08 | | | |
| Nitrobenzene | 0.41 | 0.32 | 1.20 | | | |

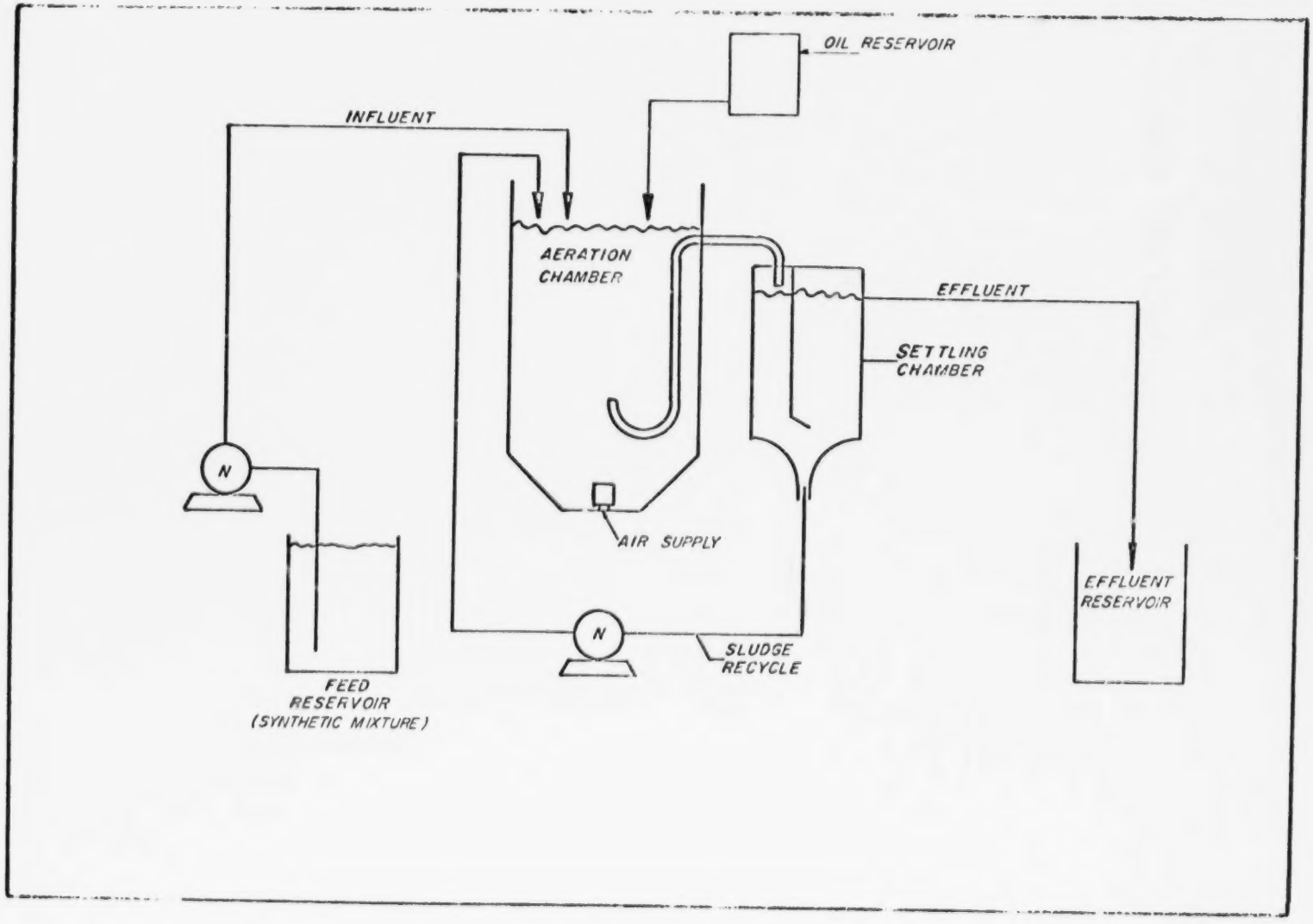
(1) grams $BOD_5$/gram substrate.
(2) grams COD/gram substrate.
(3) grams total oxygen/gram substrate
(4) recovered from water
(5) recovered directly
(6) erratic data.

Vegetable oil had the highest density and was most readily degraded by hexane extraction. The refinery waste oil had the lowest density, was the least viscous, and was the most difficult to extract in hexane. The other tests showed that the vegetable oil had the highest five-day BOD, while the crude oil had the highest COD. In addition, the long term Warburg experiments demonstrated that metabolizing the vegetable oil required more oxygen than the other compounds. The COD results for benzene were very erratic, demonstrating the limitation of this test as a method for monitoring benzene.

## Study Systems

### Activated Sludge

The majority of the experiments involved the comparison of performance in related small scale activated sludge systems. A typical system is shown schematically in Figure 1, and consists of a 6.8 liter cylindrical aeration tank followed by a solids clarification unit. Diffused air was pumped continuously into the base of the reactor to provide both turbulent conditions and a source of oxygen. The test oil material and sewage were fed to the aerated vessel at the top of the tank. The effluent line from the reactor was placed in the middle of the reactor, four inches from the bottom, and served to minimize any short circuiting in the system. The biochemical products leaving the reactor flowed into the clarification unit




SCHEMATIC OF BIOLOGICAL UNIT

FIGURE 1

where the heavier microbial floc settled out. The microorganisms were recycled to the reactor continuously, and could be wasted from the system, if desired. The clarified effluent was collected in a graduated reservoir to check the volumetric flow rate and to examine the effluent characteristics. In addition to the usual measurements to evaluate performance in these systems, special attention was directed toward the oxygen utilization rate and settling properties of the sludge. The method of analysis employed in these investigations is presented in the Appendix to the report.

Instead of using an "actual" domestic waste as the primary food source, a synthetic mixture was prepared daily. This mixture was selected in order to minimize the problems of concentration variance and the possibility of objectionable compounds interfering directly with the system performance. The inconsistent composition of a domestic waste due to unexpected disturbances, such as shock loads and normal variations in the domestic load, could dampen out oil effects on a biological system. The composition of the synthetic mixture is given in Table 2, and includes sources of protein, carbohydrates, amino acid, ammonia, phosphate, and other basic nutrients:

TABLE 2

SYNTHETIC DOMESTIC WASTE COMPOSITION
FOR A BOD OF 100,000 MG/L*

| Ingredient | grams/liter |
|---|---|
| skim milk | 48 |
| peptone | 48 |
| gelatin | 16 |
| soluble starch | 32 |
| urea | 8 |
| disodium hydrogen phosphate | 8 |
| KCl | 1.12 |
| $CaCl_2$ | 1.12 |
| $MgSO_4$ | 0.80 |
| $Fe_2(SO_4)_3$ | 0.80 |
| $NH_4Cl$ | 8 |

*The characteristics of synthetic sewage have been presented in Table 1.

Samples were diluted to the strength shown in the various studies.

## Respirometer Systems

In order to explore certain phenomena that could not easily be investigated on a continuous basis, respirometer studies were performed. The respirometer measurement systems utilized in the project included the Gilson system and the Warburg system.

The Gilson respirometer shown in Figure 2 is described by its manufacturer as "a differential respirometer, in which environmental fluctuations can be minimized by the manifold connecting the reference flask and the sample flasks". The system is designed to eliminate the variations in readings due to temperature and atmospheric pressure changes. Pressure differences from oxygen utilization in the sample flask are monitored using an internal manometer connected to a micrometer. This device is capable of measuring a pressure difference of one microliter. A valve on the manifold and one connecting the two legs of the manometer regulate the resupply of oxygen to the sample flasks. The manometer is constructed of plastic and uses a mixture of kerosene and Sudan Red III as the manometer fluid. A system of capillary tubing connects the manometer to the sample flask. The flask is controlled from variations in atmospheric temperature by a thermally controlled water bath.

The Warburg system shown in Figure 3 is the standard manometric apparatus used to measure oxygen utilization. The pressure difference or oxygen utilization is measured directly from the graduated manometer which uses "Brodie" solution as the manometer fluid. A pressure difference of 1 mm can be measured in this system. The flask is refurnished with oxygen by opening the valve at the top of the manometer unit. A water bath system controls the temperature within $\pm$ 0.1° C.

The basic difference between the two respirometer systems is that for the Warburg apparatus, the sample flasks are independent from the other flasks in the system. Control flasks containing only distilled water with potassium hydroxide in the center well are used to determine the changes in environmental conditions. These observations are then subtracted from the sample flask readings in order to yield the true biochemical uptake.

Calculation of the oxygen uptake rate and accumulation was carried out using an IBM 1130 computer. Programs were developed to compute both the rate of oxygen utilization for an average period of time and the total oxygen demand. For a small increment of time, the rate of oxygen utilization was determined from the slope of a straight line least square analysis of the pressure differences observed for this time period. These rates were then plotted as the dependent variable in an X-Y coordinate system with the corresponding

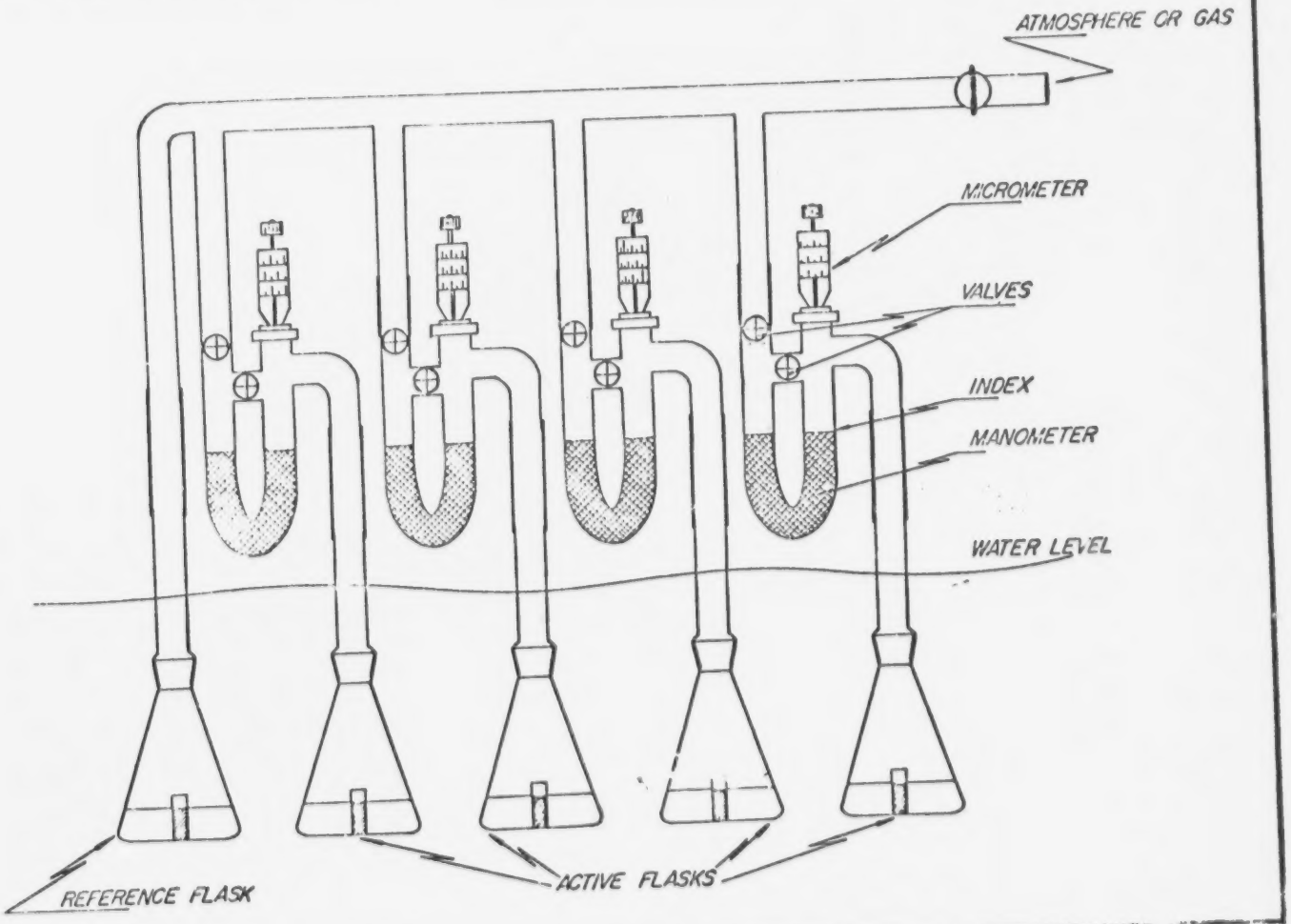
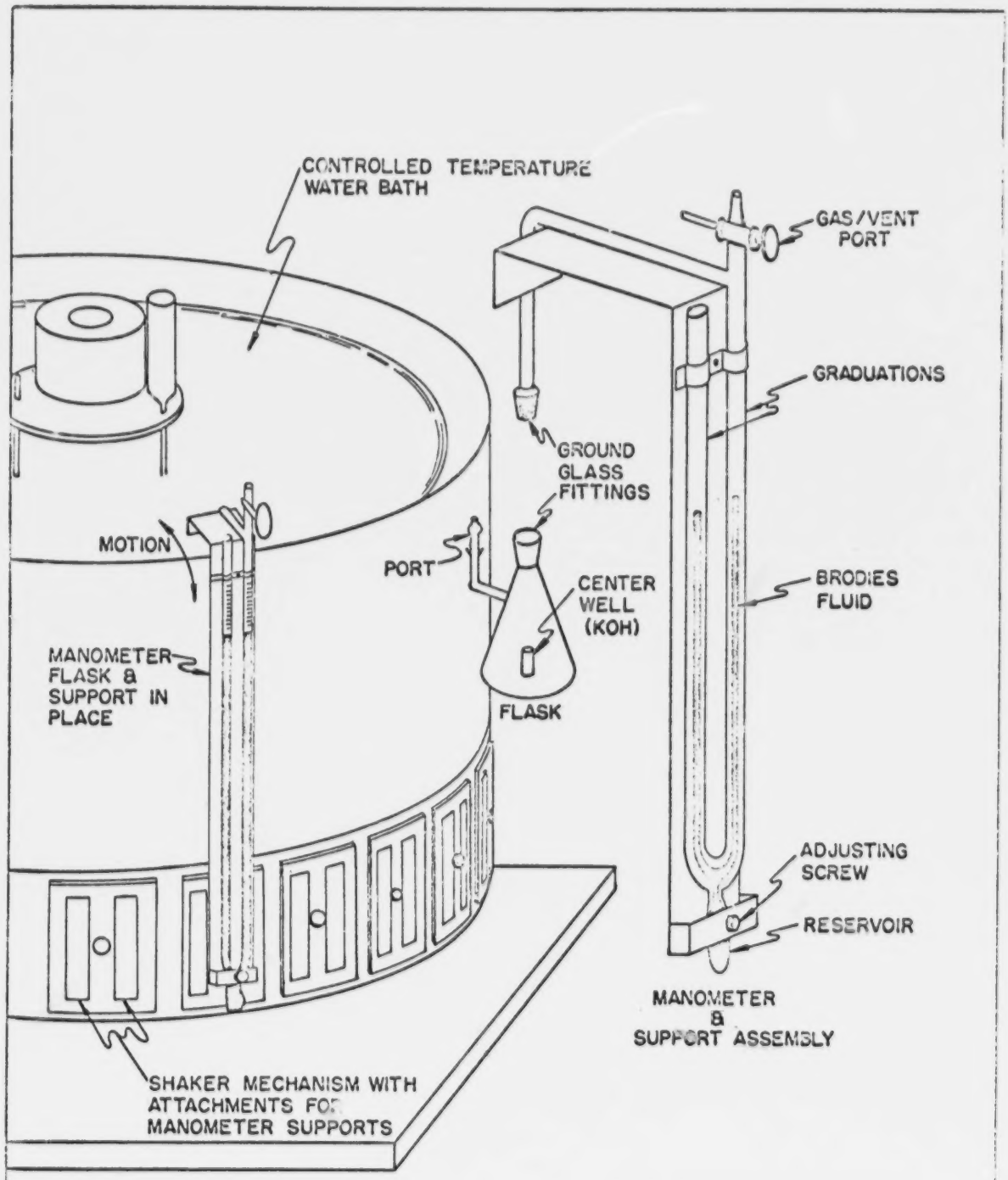



FIGURE 2
DIFFERENTIAL RESPIROMETER SYSTEM WITH SINGLE REFERENCE FLASK




WARBURG APPARATUS

FIGURE 3

cumulative time period as the independent variable. The area under this curve, computed using the trapazoidal rule, was the cumulative oxygen demand.

## Difficulties In The Experimental Studies

The principle reason so little information is available on the behavior of oily materials in biological systems is the extreme difficulties involved in working with these compounds and in measuring them. In order to understand the method of procedure employed in the studies and to evaluate the validity and limitations of the experimental results, it is necessary to fully appreciate the experimental problems associated with the test materials.

The principal study difficulties were encountered in two areas. The first area was the method of simulating the introduction of low concentrations of the high molecular weight compounds into the test systems. Since the materials were insoluble, they could not be mixed with the basic sewage in the receiving well. If this were done, the materials would tend to collect on the walls of the reservoir, or at the liquid surface, and would not enter the system under any known or definable flow rate. To overcome this problem, it was decided that the test oils would be introduced into the system separately from the sewage. The method that was chosen was to drip these materials directly into the aeration chamber. Investigations showed that, if the flow rates could be controlled at a low enough level, the materials would become involved in the mixed contents of the tank. The principal concern, however, was the feed rate. For example, considering the volume of the aeration tank as six liters, one would calculate that the average sewage flow for a six hour detention time is 1.0 liters/hour. Under these conditions, an oil feed rate of 1 ml/hour is equal to approximately 900 mg/l. Feed rates below 1 ml per hour were extremely difficult to achieve with any degree of accuracy or control. Study of this problem resulted in the development of a system where the flow rates were controlled by discharge to the system through capillary tubing. In order to overcome the difficulty of the long lengths of capillary tubing involved, a "spaghetti" type tubing (Teflon – TFE) Fluorocarbon Resin, a registered trademark of E.I. duPont de Nemours and Company) was obtained. Employing this type of material in coils it was possible to obtain capillary lengths as long as twenty to thirty feet. The oil could then be prepared in a burete and allowed to flow through this capillary tubing. Flow rates in the order of less than 0.05 ml/hour could be measured accurately in such a system. Operating at these flow rates it was then possible to simulate low concentration systems.

The volumetric flow rates ranged from 0.7 ml/day to 32 ml/day and depended upon the diameter (0.25 to 0.5 mm) and length (6 inches to 20 feet) of the tubing. These feed systems were checked frequently in order to maintain the designed flow rate and were constructed in duplicate in order to provide standby systems in case of failure.

The second, and by far the more serious, problem concerned the measurement and identification of the hydrocarbons. Although the petrochemical industry has developed many analytical methods, virtually none are applicable to the conditions encountered in biological systems. The method of analysis standardly employed in "sanitary analysis", the extraction in hexane or a similar solvent with subsequent gravimetric determination, is inaccurate and provides neither insight into the nature of change of compounds nor the ability to separate various compounds one from the other. Tests such as BOD, COD, and the like are similarly of limited value in providing any substantial information on change of the primary study substrates.

A detailed study, described in the Appendix to the report, investigated the use of a gas/liquid chromatography as a more subtle method of analysis. Although the procedures developed were quite applicable to low molecular weight compounds, it was not possible to develop a satisfactory method of separation and identification of heterogeneous high molecular weight materials. The study did develop methods of sample collection and extraction which can form the basis for a continued investigation of the phenomena.

Presented with the difficulty of having no direct way to measure the test compounds, the study relied primarily on indirect measurements related to the biological population. The most important indicators were the oxygen utilization rate of the biological mass, and the sludge settling properties. In addition, microscopic examination of the microbial population and measurement of the ability of the biological system to utilize other test substrates, such as the synthetic sewage, were employed to describe system conditions.

Finally, an observation must be presented on the ability to perform a reasonable mass balance of any of the systems under study. The nature of the primary test compounds is such that any contact with a surface results in adsorbtion of material and a subsequent loss from the system. In systems as complex as the continuous flow treatment system, normal study procedures resulted in apparent losses of materials as high as 40%. Even under conditions where extreme care was exercised, as much as 20% of the test material would be unaccounted for in the study.

The impact of the problems outlined above limits the precision of measurement with respect to the primary compounds. It was possible, however, through repeated experimentation and careful use of preferential experiments to accurately define the influence of the material on the physical and biological systems investigated.

## INITIAL STUDIES

### Study Purpose

The goals of the initial studies were to determine how significantly the test compounds interferred with activated sludge; to examine how this interference was caused, and if it could be eliminated by system operation. Questions relating to the biodegradability of the compounds and the effect of emulsification agents and temperature on biodegradability were also explored in this study sequence.

### Activated Sludge Studies

Six continuous systems were set up and acclimated to synthetic sewage for two weeks. After the systems had come to balance and were all achieving in excess of 90% BOD reduction, the test substrates were introduced into the systems. Vegetable oil, crank case oil, and benzene were studied and the pertinent data is presented in Table 3.

In the benzene study, since the substrate was soluble, it was mixed with the sewage in the receiving well. The influent strength reflects both the sewage and the test substrate. The results indicated that after a short acclimatization period, the system performed essentially the same as the control unit, with the exception that the uptake rate was lower. The lower oxygen use was traced, in part to the stripping of the benzene.

In the case of the oils, it was not possible to add the substrate to the sewage feed, so they were introduced from a capilliary drip system. The influent strength measurements do not reflect the test substrate effect.

The introduction of the oils had an immediate impact on the systems. This impact was most noticeable in the settling properties of the sludges. Figure 4 shows the comparative settling data for the control and the vegetable oil units. Similar results were obtained for the crank case oil.

The loss of settling properties resulted in a very high effluent suspended solids from the system, and complete system failure. To maintain treatment, solids were externally separated and returned to the system. Under such conditions, the systems could continue to operate and be observed. Although the data is quite difficult to interpret, it is clear that the bacterial system did not lose its ability to assimilate organics, since the filtered effluents from the oil units are

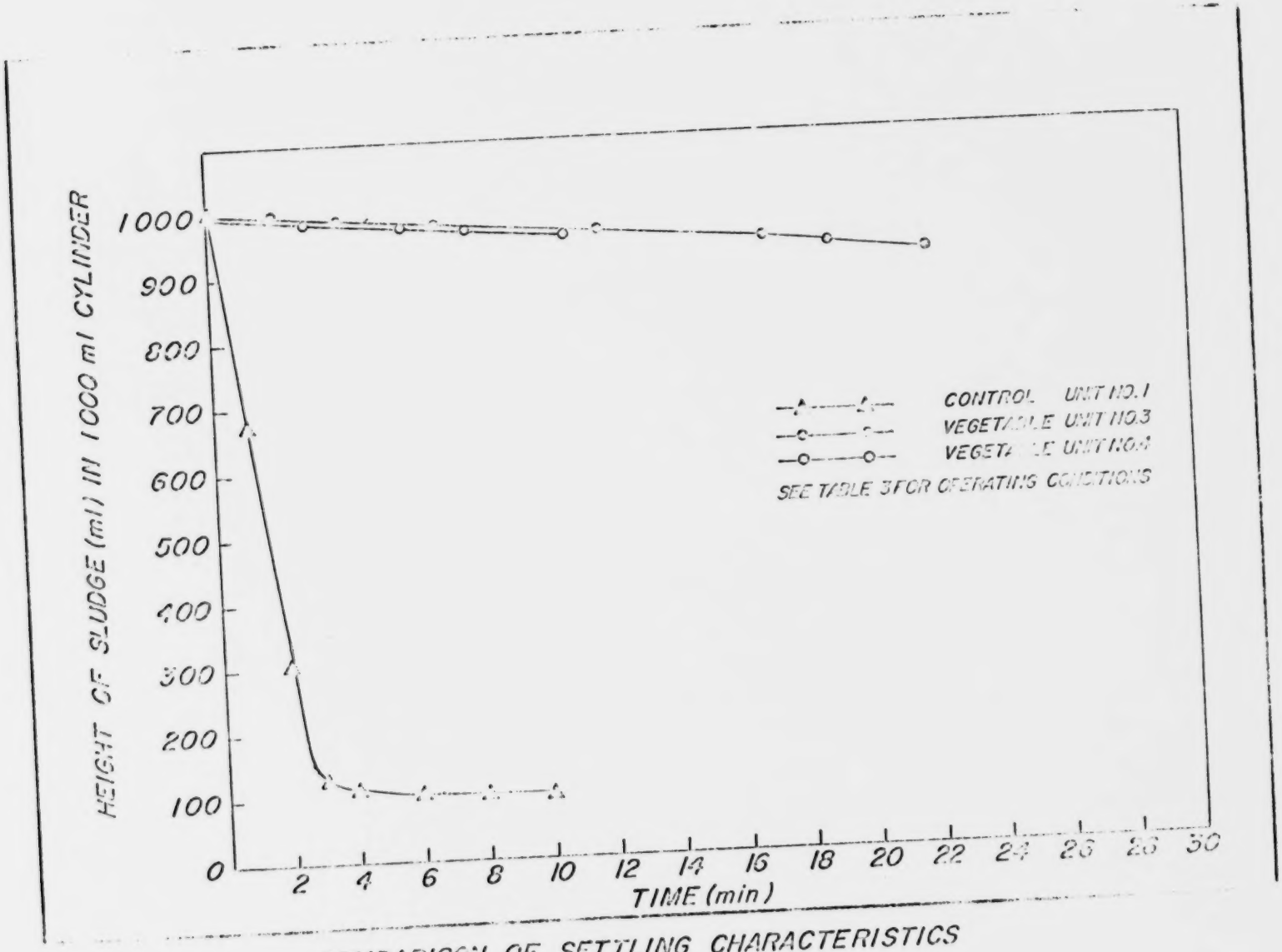
TABLE 3

INITIAL ACTIVATED SLUDGE STUDIES

| Unit Number | Control | Crank Case Oil | Vegetable Oil | Vegetable Oil | Benzene | Benzene |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Sewage BOD mg/l | 308 | 308 | 308 | 308 | 262 | 313 |
| COD mg/l | 452 | 452 | 452 | 452 | 350 | 346 |
| Substrate (mg/l) Concentration | | 711 | 1,100 | 793 | 50 | 500 |
| Hexane Solubles (mg/l) | | 585 | 980 | 710 | | |
| Detention Time (hours) | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 |
| MLSS | 2,313 | 2,524 | 2,692 | 2,621 | 1,959 | 2,300 |
| Oxygen uptake rate mg/l/hr | 50 | 46 | 65 | 45 | 34 | 37 |
| Effluent $BOD_1^1$ mg/l | 10 | 14 | 10 | 61 | 13 | 17 |
| $COD^1$ mg/l | 33 | 55 | 45 | 90 | (2) | (2) |

(1) Filtered samples

(2) Erratic data.




COMPARISON OF SETTLING CHARACTERISTICS

FIGURE 4

quite similar to the control. (This is not true in the #4 unit, where some interference was observed.) It is also notable that little increase in oxygen use is noted in the systems. The test compounds seem to seriously affect the physical properties of the sludges, but otherwise have a limited effect.

After approximately four (4) weeks of operation, these systems were discontinued in favor of lower loading studies where more detailed analyses could be performed.

## Sludge Settling Studies

Detailed settling studies were conducted on all test units. The results of these studies as well as all other settling data collected in the study is considered in a separate section appearing later in the report.

## Respirometer Studies

In addition to the continuous systems studies, batch studies employing the Gilson and Warburg respirometer were conducted. The studies included investigation of the ultimate oxygen demand of each test compound; studies into the effect of temperature and emulsifying agent on biological activity; and examinations of the biodegradability of a select group of benzene derivatives. Similar to the BOD technique, a respirometer may be used as a method of determining the overall biochemical strength of a waste sample. The biochemical phenomena observed in the respirometer flask are explored in the Theory section of the Appendix. This discussion emphasizes the basic mass transport occurring in this type of system.

The continuously mixed biological unit shown in Figure 5 typifies the respirometer flask. The gas phase contains the reservoir of oxygen needed to metabolize the substrate. The microbial population, nutrients including oxygen and ammonia, and substrate are the principal components of the liquid phase. The cylindrical center well is a reservoir for potassium hydroxide, which is used to absorb the carbon dioxide produced by the biochemical reaction. As the bacteria use the test substrate, oxygen is utilized creating a concentration gradient between the gas and liquid phase. This driving force in the direction of the liquid phase causes a decrease in the amount of oxygen in the flask. This change in pressure is directly related to oxygen utilization. The rate of oxygen utilization can be continuously monitored and determined. The cumulative utilization of oxygen can also be determined from a continuous monitoring of pressure differences in a manometric flask.

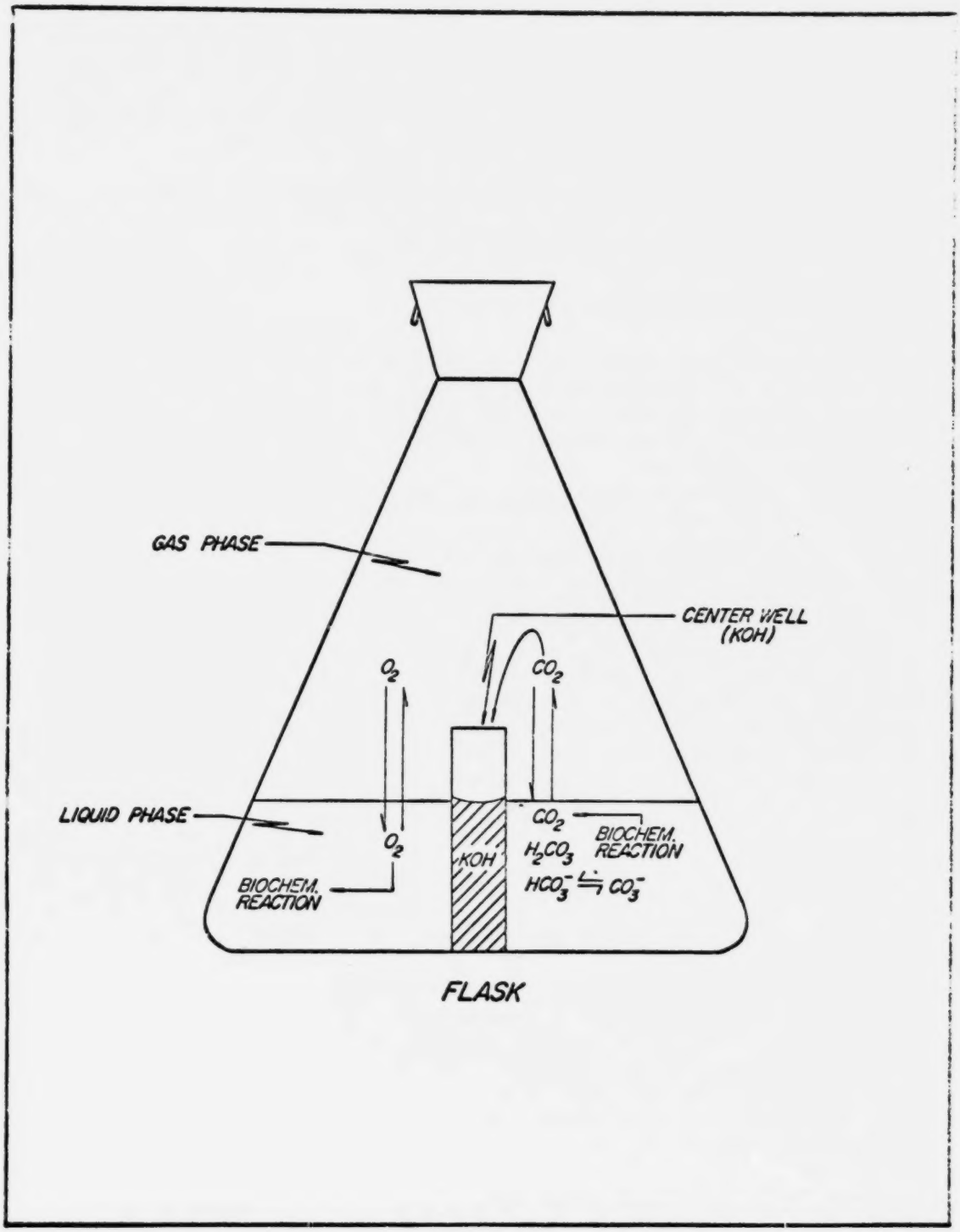



FIGURE 5
SCHEMATIC REPRESENTATION OF WARBURG RESPIROMETER

## Experimental Results

The experiment involved the examination of:

1. the quantity of oxygen utilized per gram of test material added;
2. the effect of emulsifying agents on the biodegradation of hydrocarbons;
3. the effect of temperature on removal of test material;
4. biodegradability of some simple benzene derivatives.

The first series of experiments using the Warburg respirometer were conducted to determine the ultimate oxygen demand of the test materials. The experiment was run for approximately one month and examined the test materials as sole sources of organic material for the microorganisms. In all, three respirometer experiments were conducted for initial concentrations that ranged as follows:

1. crank case oil: 325 to 450 mg/l
2. crude oil: 302 to 550 mg/l
3. waste oil: 420 to 450 mg/l
4. vegetable oil: 265 to 720 mg/l

For each respirometer study, seven flasks were used and included a control flask, a seed flask, and five test flasks. In each flask, a known mass of test material was mixed with a seed acclimated in the continuously fed oil unit and was suspended with dilution water which contained the basic nutrients. An emulsifying agent was not provided in this phase of the study. The average oxygen utilization is presented in Table 4. The vegetable oil seemed to be the easiest to degrade; the ratio of grams of oxygen utilized to grams of oil added being 2.06. All the substrates exhibited oxygen utilization indicating that a fraction of the hydrocarbon was metabolized in each case; however, the time required for oxidation was very long. As a consequence of the limitations described elsewhere in this report, studies using the gas chromatograph could not be conducted to determine the degree of biodegradability of the test material. Sample sizes of 40 ml limited

the use of the hexane extraction procedure as a means of monitoring the removal of organic materials.

TABLE 4

LONG TERM WARBURG STUDIES ON THE INSOLUBLE TEST MATERIALS

| Substrate | Total Oxygen Utilized (mg/l) | Substrate (mg/l) | grams oxygen used / grams substrate added | Average Rate (ppm/hr) | Maximum Rate (ppm/hr) |
|---|---|---|---|---|---|
| Crank Case Oil | 466 | 400 | 1.16 | 1.34 | 7.87 |
| Crude Oil | 397 | 385 | 1.03 | 1.10 | 4.28 |
| Refinery Waste | 522 | 430 | 1.21 | 1.80 | 2.33 |
| Vegetable Oil | 913 | 443 | 2.06 | 2.52 | 10.73 |

Data presented are average values.

## Effect Of Emulsifying Agents And Temperature

Considering the insoluble nature of the test materials and the limited biodegradation observed in the long term Warburg studies, it was suggested that the addition of an emulsifying agent may provide a means of dispersing the hydrocarbon throughout the liquid phase and increase microbial activity. The effect of temperature was also explored with the idea that increasing the temperature might increase the rate of biochemical activity significantly.

The respirometer experiments were run using the Gilson respirometer at temperatures of 20, 25, and 30°C; the test substrate was crank case oil and the emulsifying agents were anionic, cationic, and non-ionic surfactants. Each experiment was studied for approximately four days, and the primary goal of these experiments was to observe any change in the oxygen utilization rate due to the emulsifying agent and/or the temperature.

A summary of the three experiments is presented in Table 5. These data are average values and are based on total oxygen utilized in four days. The results show that for a specified temperature, the emulsifying agents had only a minor effect on the metabolism of the test material. The results also seem to indicate that the microorganiss preferentially selected the

emulsifier as the primary source of carbon instead of the hydrocarbon. This data interpretation is supported by the experiments carried out at 25 and 30°C.

An increase in the biological activity was observed with increasing temperature as demonstrated by the increase in grams of oxygen utilized per gram of material added (see column 8, Table 5). Not only was there an increase in the system with the crank case oil by itself, but similar observations were monitored for the emulsifiers alone and in combination with the crank case oil. However, the overall increase in the metabolism of the hydrocarbon with the addition of an emulsifying agent was approximately that associated with the normal increase of biological activity with temperature.

No attempt was made to use non-biodegradable emulsifiers as addition of these materials could have an adverse effect on the biochemical reaction. To reduce the inhibition, long term acclimation and toxicity studies would have had to be conducted, and such experiments did not seem warranted at that time.

## Benzene Derivatives Study

The final series of respirometer studies were conducted in conjunction with long term biochemical oxygen demand experiments to determine the biodegradability of several benzene derivatives. This step was an initial phase of a possible study to investigate the problem in a continuous flow system of benzene based compounds that were observed to be difficult to metabolize. Experiments were set up studying the biodegradability of benzene, toluene, ethylbenzene, and n-propyl benzene. The results presented in Table 6 are typical of the respirometer experiments conducted. All compounds were readily biodegradable, especially after seed acclimation. The biodegradability and oxygen utilization studies of benzoic acid, nitrobenzene, and benzyaldehyde were conducted using the BOD bottle and the results have previously been reported in Table 1. Since all the compounds were readily biodegradable, this series of experiments was terminated in favor of a more detailed examination of the removal of the insoluble hydrocarbons in biological systems.

TABLE 5

EMULSIFICATION AND TEMPERATURE STUDY
(Average Values)

| Date | Temp | Substrate | Initial Concentration Oil mg/l | Initial Concentration Emul. mg/l | Total* Oxygen Utilized mg/l | Maximum Rate (mg/l/hr) | Oxygen Req'd For Oil Removal mg | Gr. Oxygen / Gr. Oil | Gr. Oxygen / Gr. Emulsifier |
|---|---|---|---|---|---|---|---|---|---|
| 5/13/69 | 20 | Nonionic | | 62.5 | 96 | .92 | | | 1.53 |
| 6/03/69 | | Nonionic + Crank | 285 | 62.5 | 82 | .67 | (1) | | 1.31 |
| | | Anionic | | 62.5 | 54 | .71 | | | .87 |
| | | Anionic + Crank | 256 | 62.5 | 55 | .69 | 1 | .004 | .88 |
| | | Crank | 450 | | 198 | 1.05 | 198 | .440 | |
| | | Cationic | | 62.5 | 52 | .66 | | | .83 |
| | | Cationic + Crank | 233 | 62.5 | 68 | .61 | 16 | .07 | 1.09 |
| 5/27/69 | | Nonionic | | 31.3 | 57 | .94 | | | 1.82 |
| 6/03/69 | | Nonionic + Crank | 263 | 31.3 | 88 | 1.31 | 31 | .108 | 2.82 |
| | | Anionic | | 31.3 | 50 | .98 | | | 1.60 |
| | | Anionic + Crank | 254 | 31.3 | 101 | .65 | 51 | .200 | 3.22 |
| | | Crank | 252 | 31.3 | (1) | (1) | (1) | (1) | |
| | | Cationic | | 31.3 | 61 | .64 | | | 1.95 |
| | | Cationic + Crank | 236 | 31.3 | 67 | .66 | 6 | .002 | 2.14 |
| 6/25/69 | | Nonionic | | 31.3 | 151 | 3.39 | | | 4.82 |
| 7/02/69 | | Nonionic + Crank | 245 | 31.3 | 109 | .91 | (1) | | 3.42 |
| | | Anionic | | 31.3 | 56 | .67 | | | 1.79 |
| | | Anionic + Crank | 288 | 31.3 | 137 | 1.03 | 81 | .355 | 4.38 |
| | | Crank | 320 | 31.3 | 170 | 1.15 | 170 | .532 | |
| | | Cationic | | 31.3 | 79 | .87 | | | 2.52 |
| | | Cationic + Crank | 220 | 31.3 | 84 | .76 | 5 | .006 | 2.68 |

(1) Erratic data.
* Four-day values.

TABLE 6

OXYGEN UTILIZATION OF BENZENE DERIVATIVES
GILSON STUDY (2/3 - 2/6/67)

| Substrate | Initial Concentration (mg/l) | Total Oxygen Utilized (mg/l) | grams oxygen utilized / grams substrate added |
|---|---|---|---|
| Benzene | 125 | 180 | 1.44 |
| Benzene | 125 | 185 | 1.48 |
| Toluene | 100 | 53 | 0.53 |
| Toluene | 100 | 65 | 0.65 |
| Ethylbenzene | 105 | 130 | 1.70 |
| n-propylbenzene | 37.5 | 23 | 0.67 |
| Temperature = 20°C | | Total time (minutes) = 4,300. | |

Activated Sludge Performance Under Moderate Loading Conditions

The next series of continuous system studies considered the loading range where oil concentrations were thought to be critical. The activated sludge systems were acclimated for several weeks, then fed each of the test substrates, spent crank case oil, vegetable oil, waste refinery oil, and a crude oil. The systems were adjusted so that each was at the same mixed liquor suspended solids level and was producing the same filtered effluent. The overall system data is presented in Table 7, but as in the previous studies, reflects only in a limited way, the performance of the systems.

TABLE 7
CONTINUOUS ACTIVATED SLUDGE SYSTEM PERFORMANCE

| | Control Unit | Crank Case Oil | Vegetable Oil | Refinery Oil | Crude Oil |
|---|---|---|---|---|---|
| Sewage COD * | 353 | 328 | 336 | 371 | 350 |
| BOD | 323 | 301 | 316 | 327 | 330 |
| Concentration of Substrate added | | 226 | 148 | 88 | 82 |
| Material recovered as Hexane Solubles * | | 185 | 132 | 44 | 38 |
| Detention time (hours) | 6.4 | 6.8 | 6.1 | 4.3 | 7.8 |
| MLSS * | 2,233 | 2,397 | 2,175 | 2,200 | 2,320 |
| Oxygen Uptake Rate (mg/l/hour) | 50 | 46 | 65 | 72 | 50 |

TABLE 7

(continued)

| | Control Unit | Crank Case Oil | Vegetable Oil | Refinery Oil | Crude Oil |
|---|---|---|---|---|---|
| Effluent BOD * | 20 | 20 | 18 | 20 | 16 |
| COD | 57 | 91 | 57 | 59 | 52 |
| mg/l/hour oxygen for oil utilized | 0 | 2.5 | 16.0 | 0 | 7.5 |
| mg/l/hr oxygen used / mg/l/hr H.E. applied | | 0.075 | 0.68 | -- | 0.71 |

* measured as mg/l

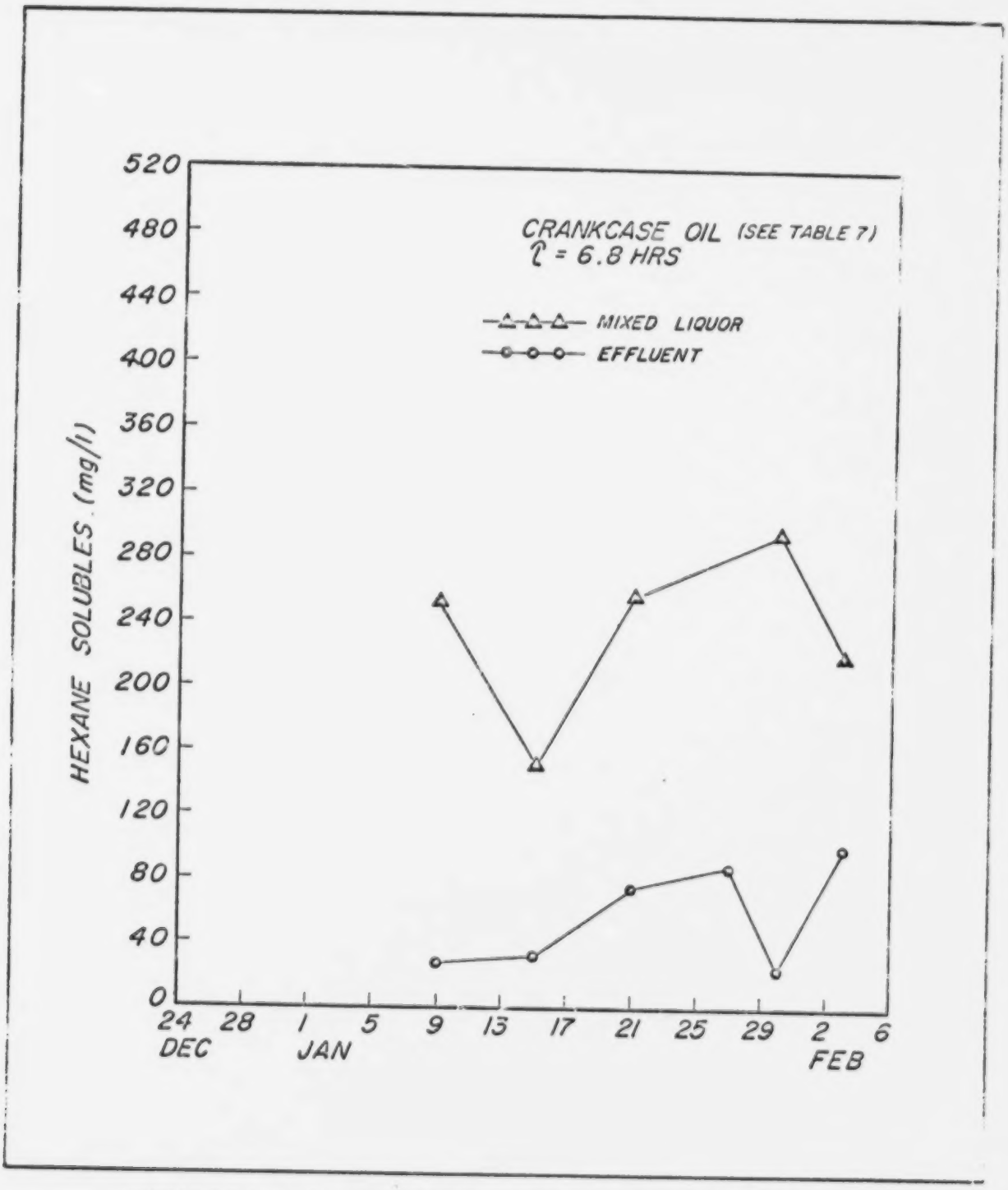
The influent strength reflects only the strength of the basic sewage. Assuming that the uptake rate associated with degradation of the sewage is constant, one can calculate the oxygen use associated with the oil compounds. This calculation has been performed and the results are presented in the penultimate row of Table 7. In the last row, the oxygen use is related to the quantity of test substrate added to the system. Little or no increased oxygen use is observed in the case of crank case or waste refinery oils.

The behavior of the crank case system can be more thoroughly understood by examining the oil content of the mixed liquor and the effluent suspended solids. Figure 6 shows the results of a hexane extraction from the mixed liquor and shows an average content of 220 mg/l with substantial variation. The effluent suspended solids shown in Figure 7 increased continually, in spite of all efforts to control them and the system is, for practical purposes, in failure during most periods.

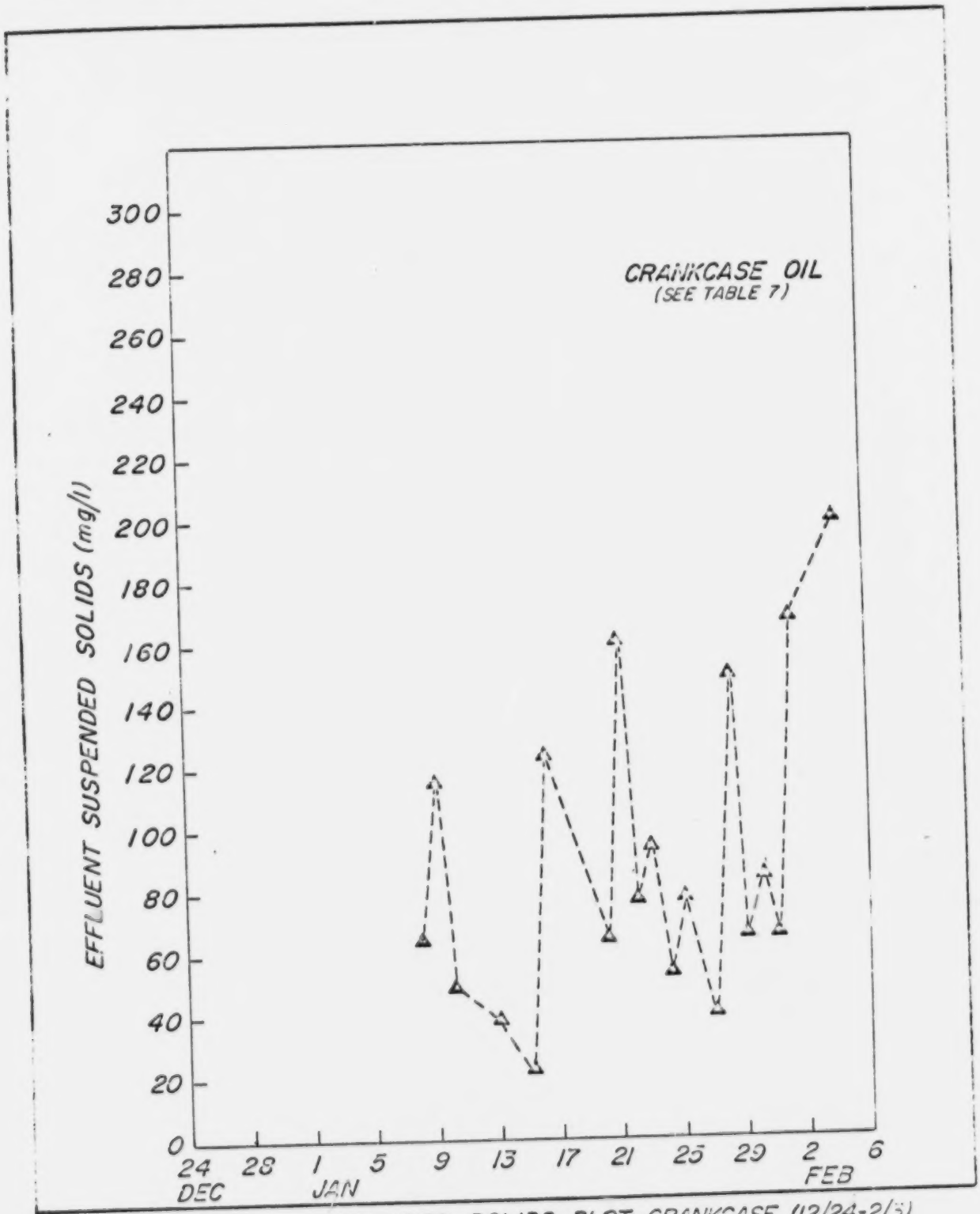
In a similar fashion, the level of oil in the sludge of the refinery waste oil system rose to a very high level, (Figure 8), and the system failed because of high effluent suspended solids.

The crude oil system is more interesting. As seen in Figure 9, the mixed liquor oil level initially reached a very high level and thereafter, decreased sharply to about 100 mg/l. Figure 10 shows the impact of this change on effluent suspended solids. The solids initially very high, reduce to an easily manageable level, as the oil content decreases.

The vegetable oil results are somewhat erratic, the effluent suspended solids vary randomly about 80 mg/l while the mixed liquor oil level, shown in Figure 11, seems to trace some




TEMPORAL HEXANE PLOT - CRANKCASE (12/24 - 2/3)
FIGURE 6




TEMPORAL SUSPENDED SOLIDS PLOT-CRANKCASE (12/24-2/3)
FIGURE 7

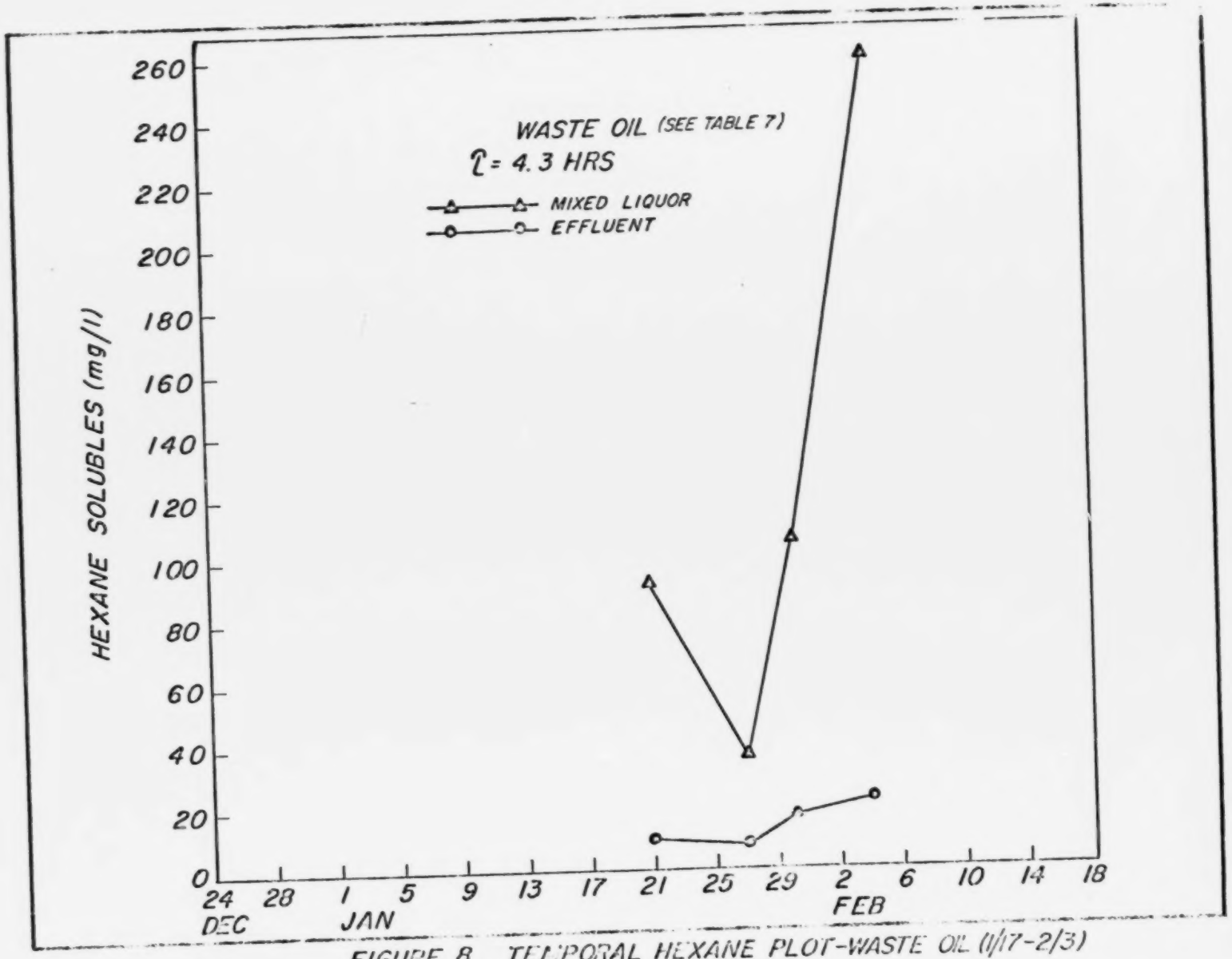
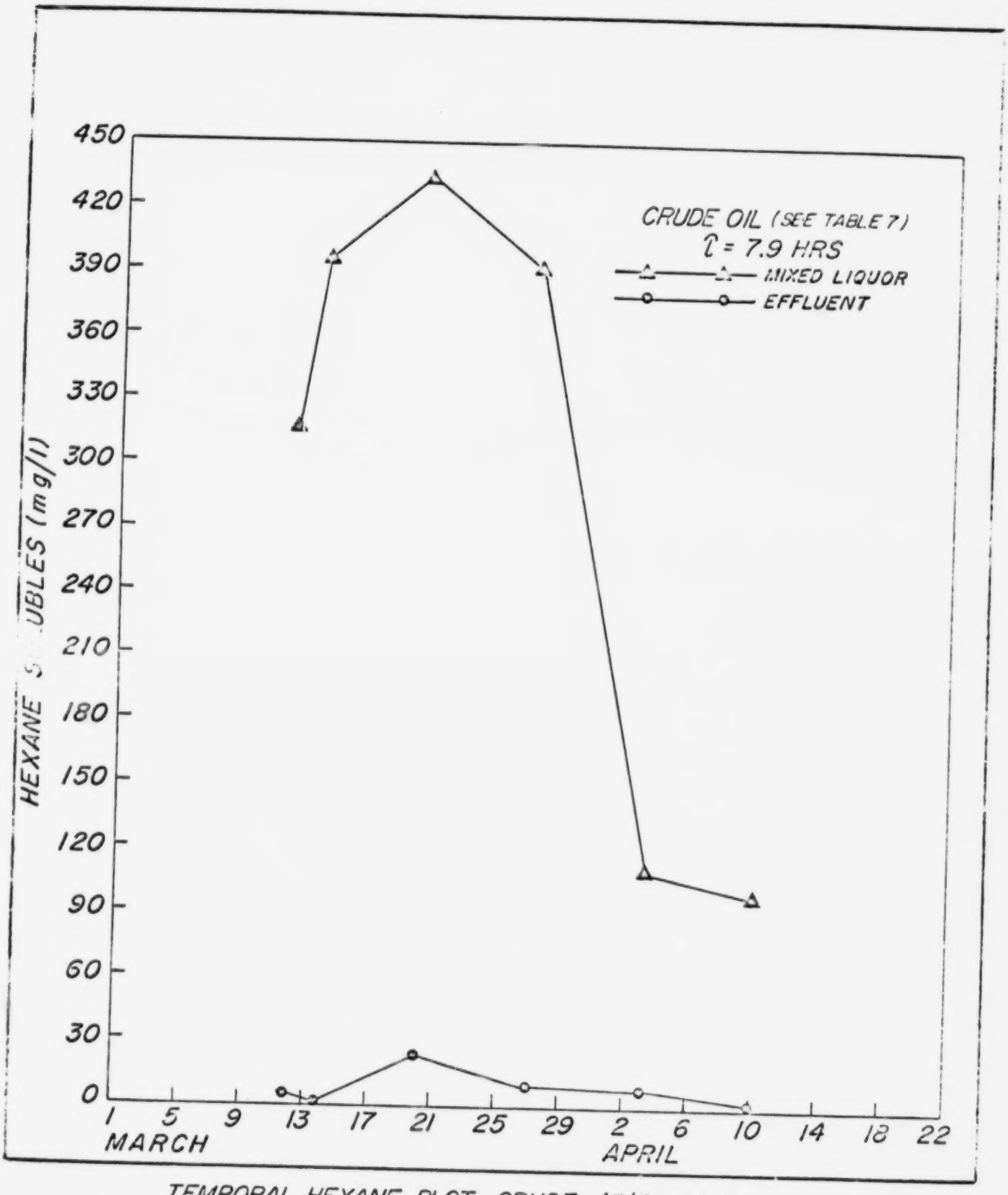



FIGURE 8 TEMPORAL HEXANE PLOT-WASTE OIL (1/17-2/3)




TEMPORAL HEXANE PLOT - CRUDE (3/5 - 4/16)

FIGURE 9

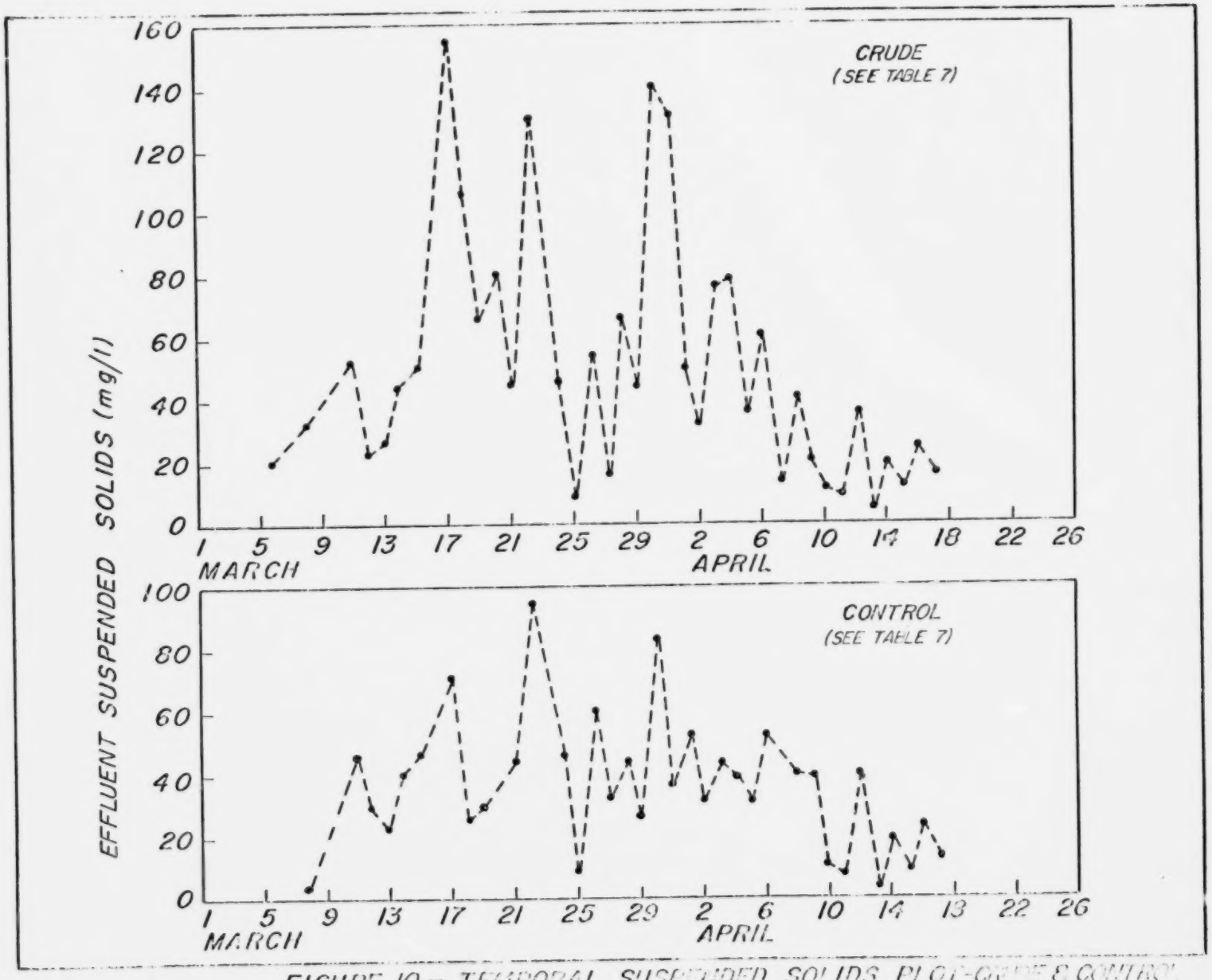



FIGURE 10 – TEMPORAL SUSPENDED SOLIDS PLOT-CRUDE & CONTROL (2/25 – 4/16)

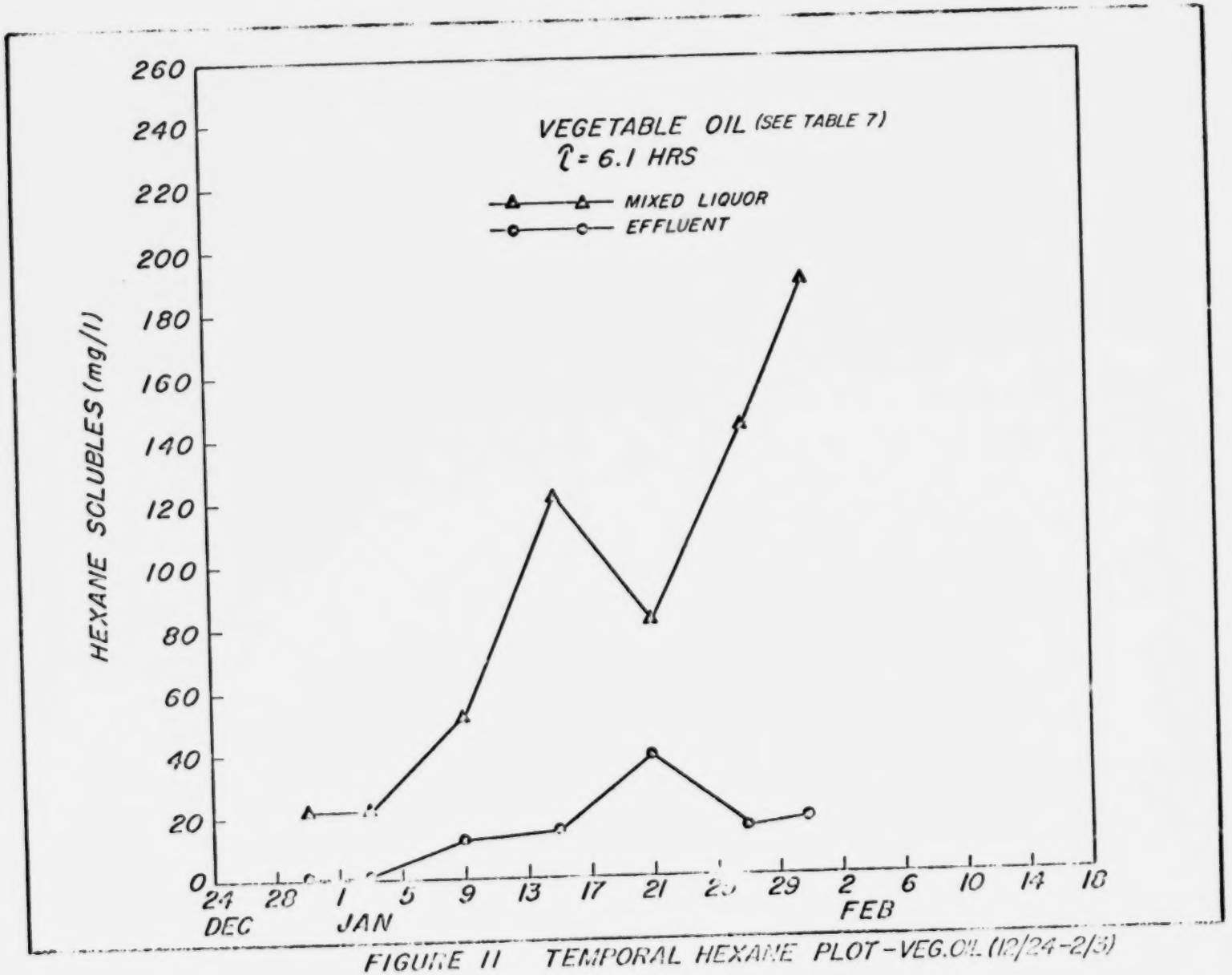



FIGURE 11 TEMPORAL HEXANE PLOT - VEG. OIL (12/24-2/3)

erratic pattern. This phenomenon was studied in some detail in the next study section.

## Reexamination of Crankcase and Return Waste Oil

To determine if it was in fact possible to treat the crankcase and waste oils, a special set of experiments were conducted. The experimental conditions were essentially the same as in the previous studies. The influent and effluent conditions are presented in Table 8, while Figures 12 through 15 present graphic demonstrations of the initial buildup and the reduction of mixed liquor oil concentration with the resulting stabilization of effluent suspended solids. The uptake rate data supports the contention that some reduction in oil content is occurring through biological oxidation.

TABLE 8

ACTIVATED SLUDGE PERFORMANCE DATA
MODERATE OIL LOADS

| | Control | Crank Case Oil | Refinery Oil | Veget. Oil | Veget. Oil | Veget. Oil |
|---|---|---|---|---|---|---|
| Sewage BOD * | | | | | | |
| COD | 349 | 353 | 351 | 351 | 295 | 382 |
| Substrate Concentration * | | 40 | 58 | 33 | 36 | 22 |
| Hexane solubles * | | 33 | 29 | 30 | 32 | 20 |
| Detention time | 7.8 | 7.3 | 7.6 | 7.5 | 6.5 | 4.0 |
| MLSS * | 2,259 | 2,278 | 2,307 | 2,495 | 2,165 | 1,465 |
| Oxygen Uptake Rate (mg/l/hour) | 48 | 52 | 55 | 67 | 57 | 43 |
| Effluent BOD * | | | | | 20 | 13 |
| COD | 67 | 52 | 58 | 46 | 56 | 46 |

* measured as mg/l.

## Additional Vegetable Oil Studies

The data collected during the final tests in this series are also reported in Table 8. The study considered a variety of systems treating vegetable oil at various solids levels and detention times. The study was intended to examine the variability of response observed with vegetable oil in earlier

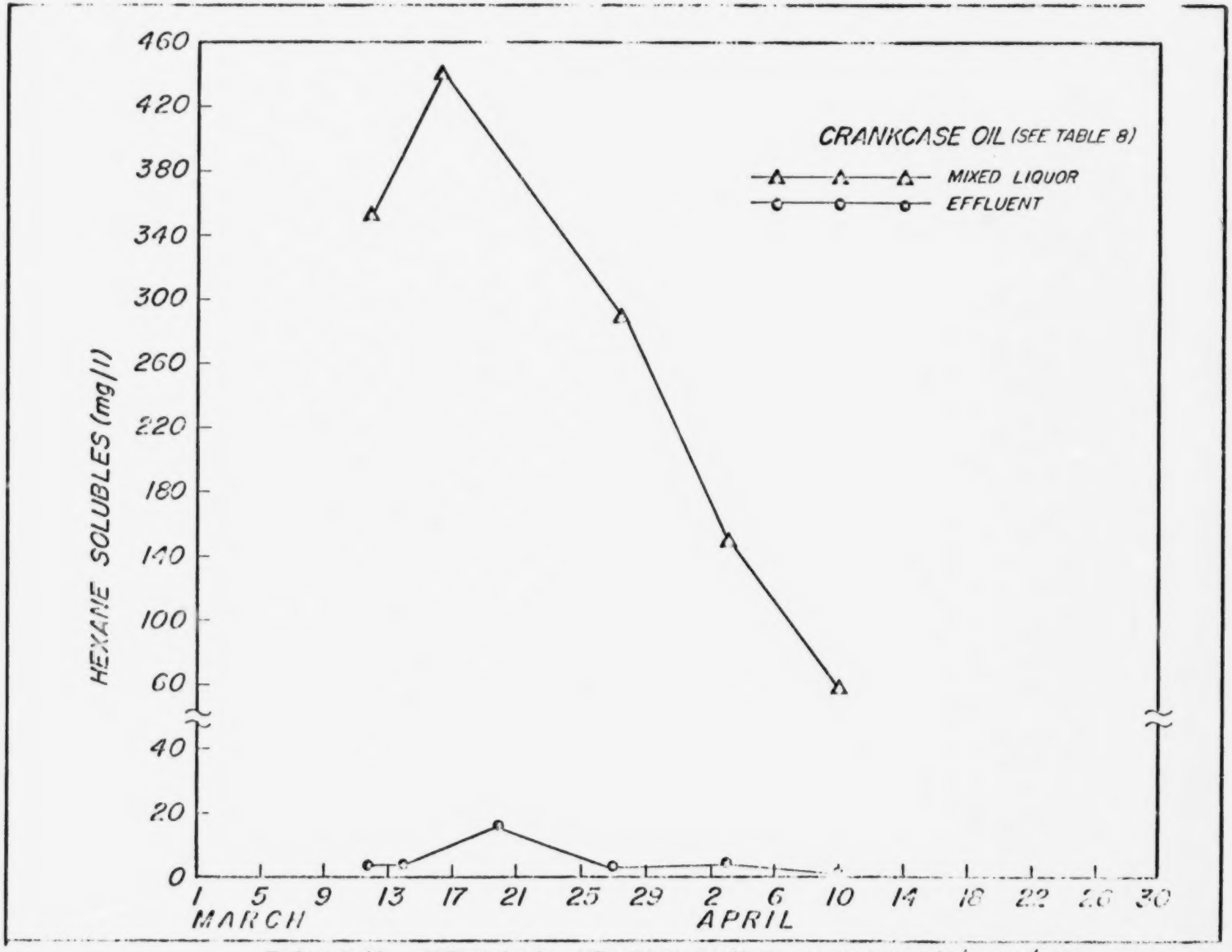
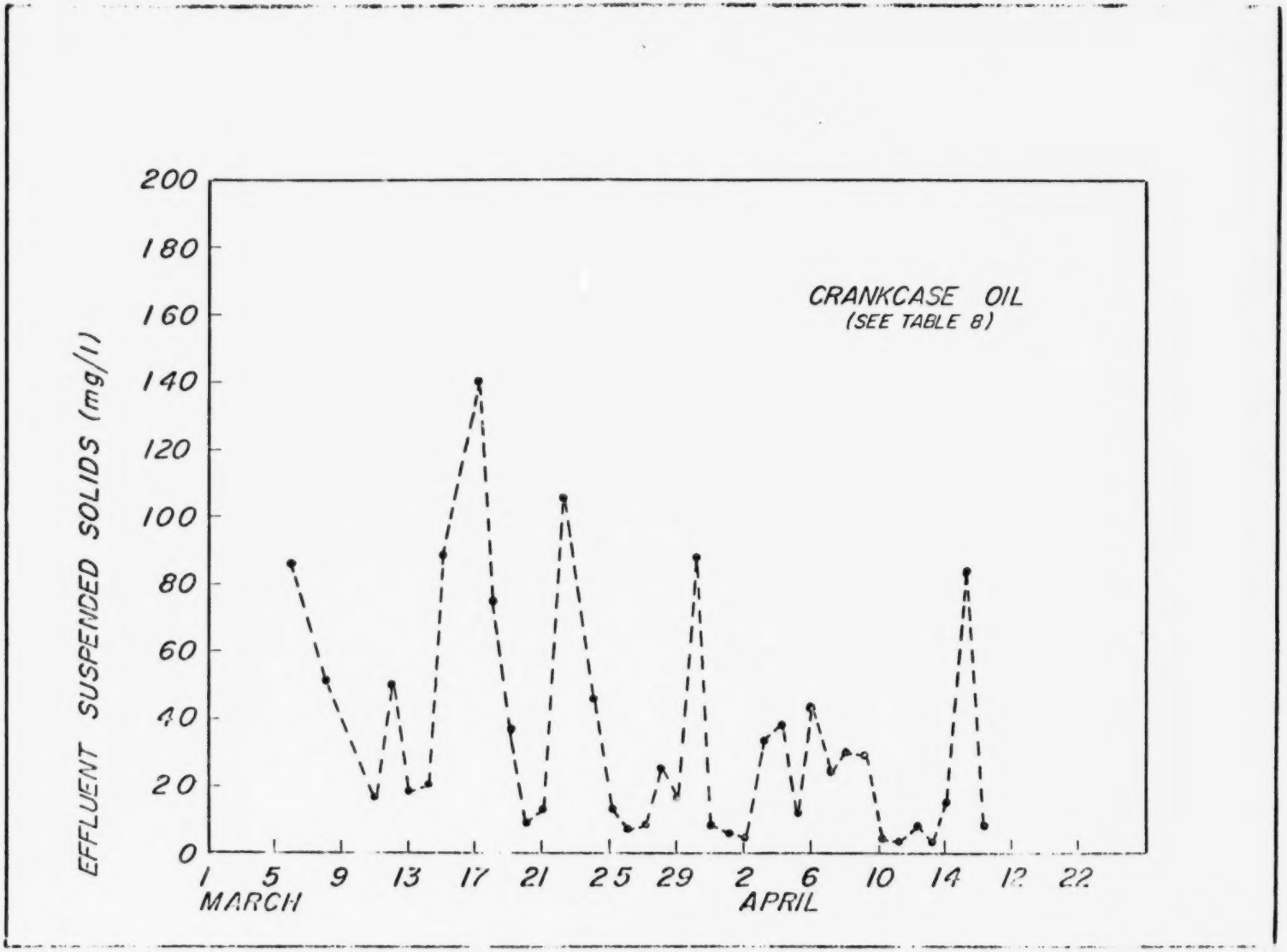
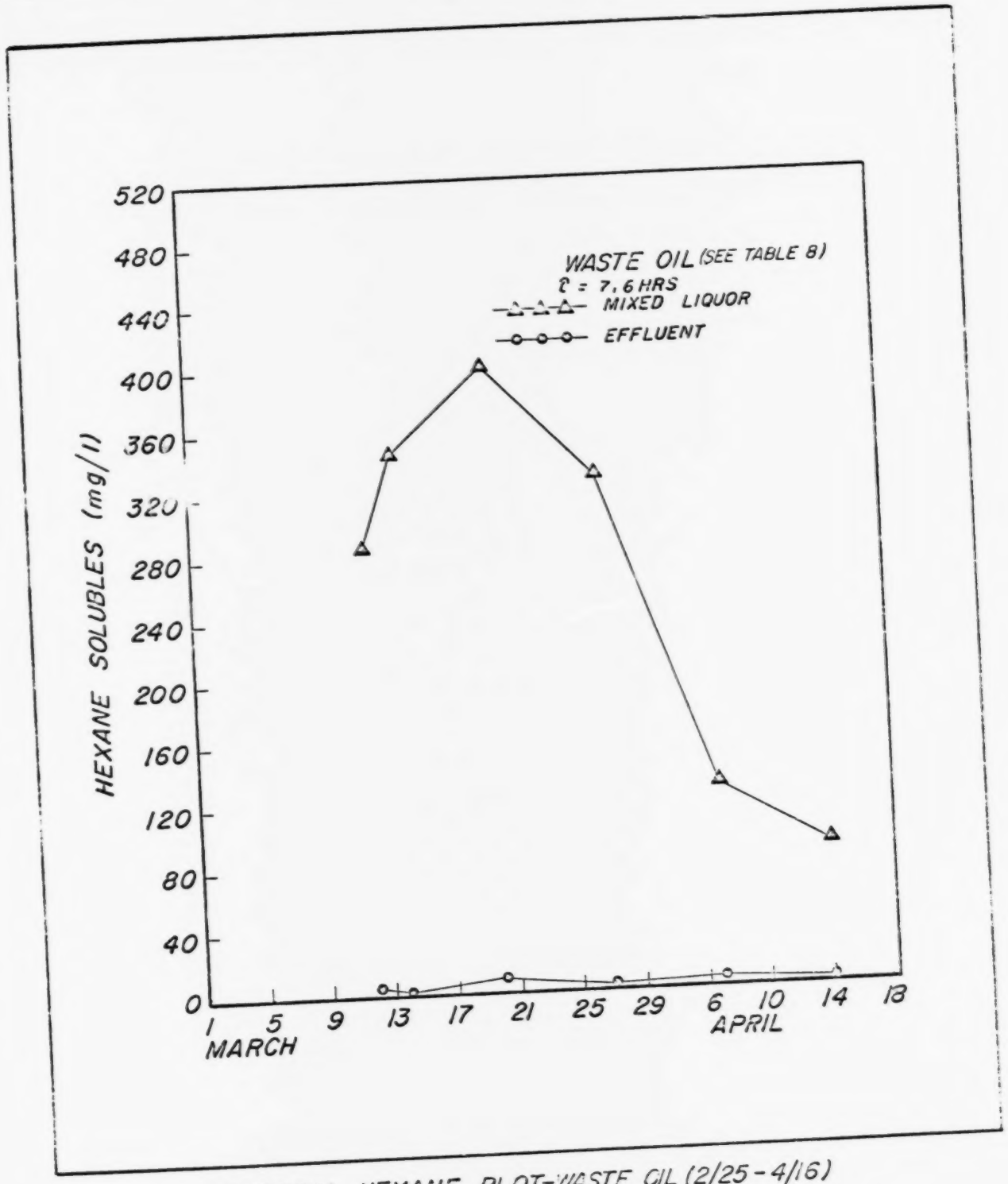



FIGURE 12- TEMPORAL HEXANE PLOTS-CRANKCASE (2/25-4/16)



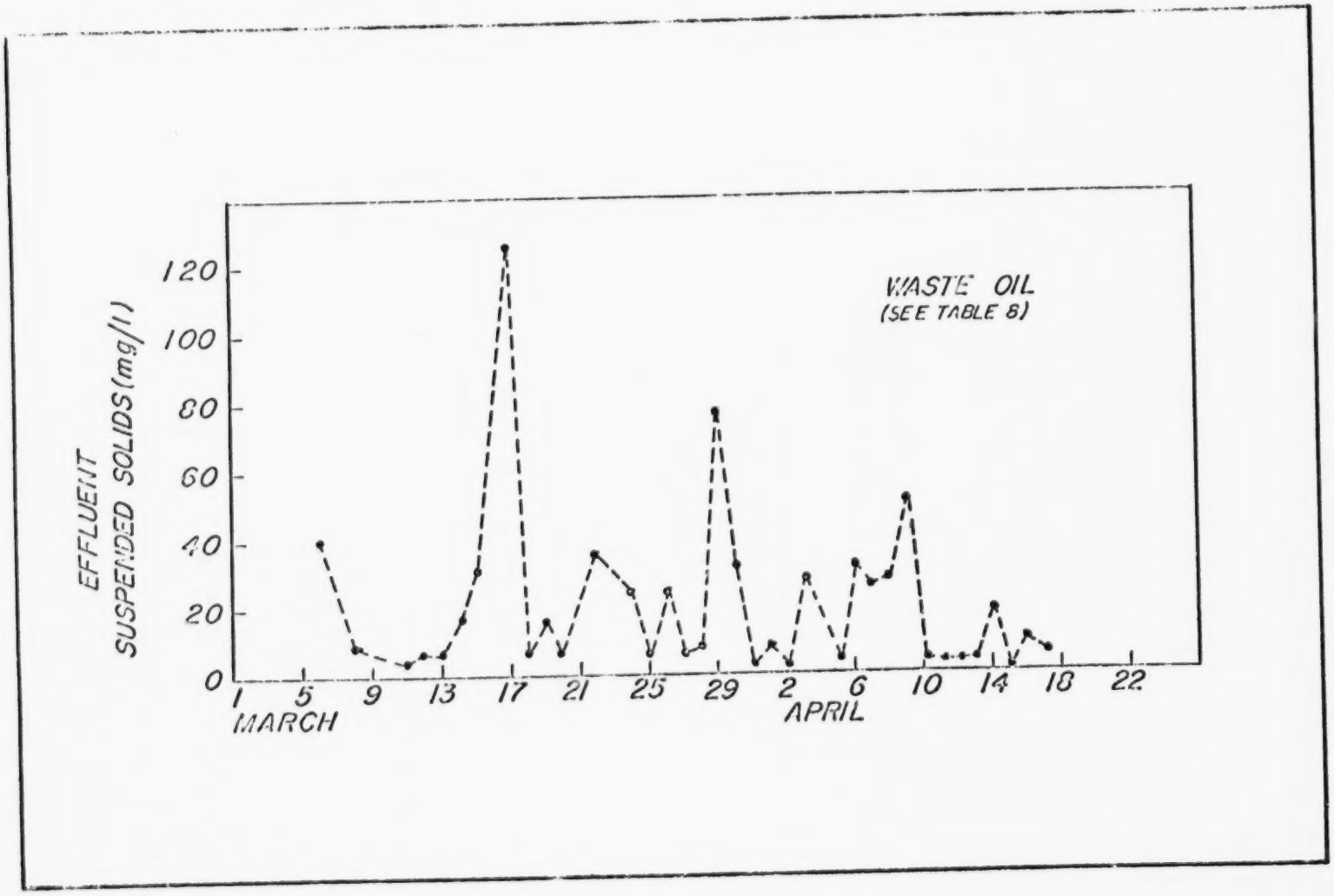

TEMPORAL SUSPENDED SOLIDS PLOT-CRANKCASE OIL (2/25-4/16)

FIGURE 13




TEMPORAL HEXANE PLOT-WASTE OIL (2/25 - 4/16)

FIGURE 14




TEMPORAL SUSPENDED SOLIDS PLOT-VEG. & WASTE (2/25-4/16)

FIGURE 15

studies. The systems in the early stages showed the typical buildup and the decline of mixed liquor oil content and then settled down to low levels. The pulsation of effluent suspended solids continued throughout the study. The reason for the seemingly erratic behavior is unknown, but a possible reason is suggested in the section dealing with sludge settling properties.

## Ancillary Studies

The final series of continuous flow experiments were designed to explore other phenomena which could provide additional insight into the performance of biological systems. The experiments involved the following:

1. An investigation of the effect of detention time on the performance of a biological system which is fed oil;

2. An attempt to acclimate a biological population to crude oil as the primary substrate;

3. A study of the response of a biological system to shock loads of crank case and refinery waste oils;

4. The behavior of a system with a primary substrate other then sewage.

Acclimation and sample analysis were conducted employing techniques similar to those previously defined in the other studies.

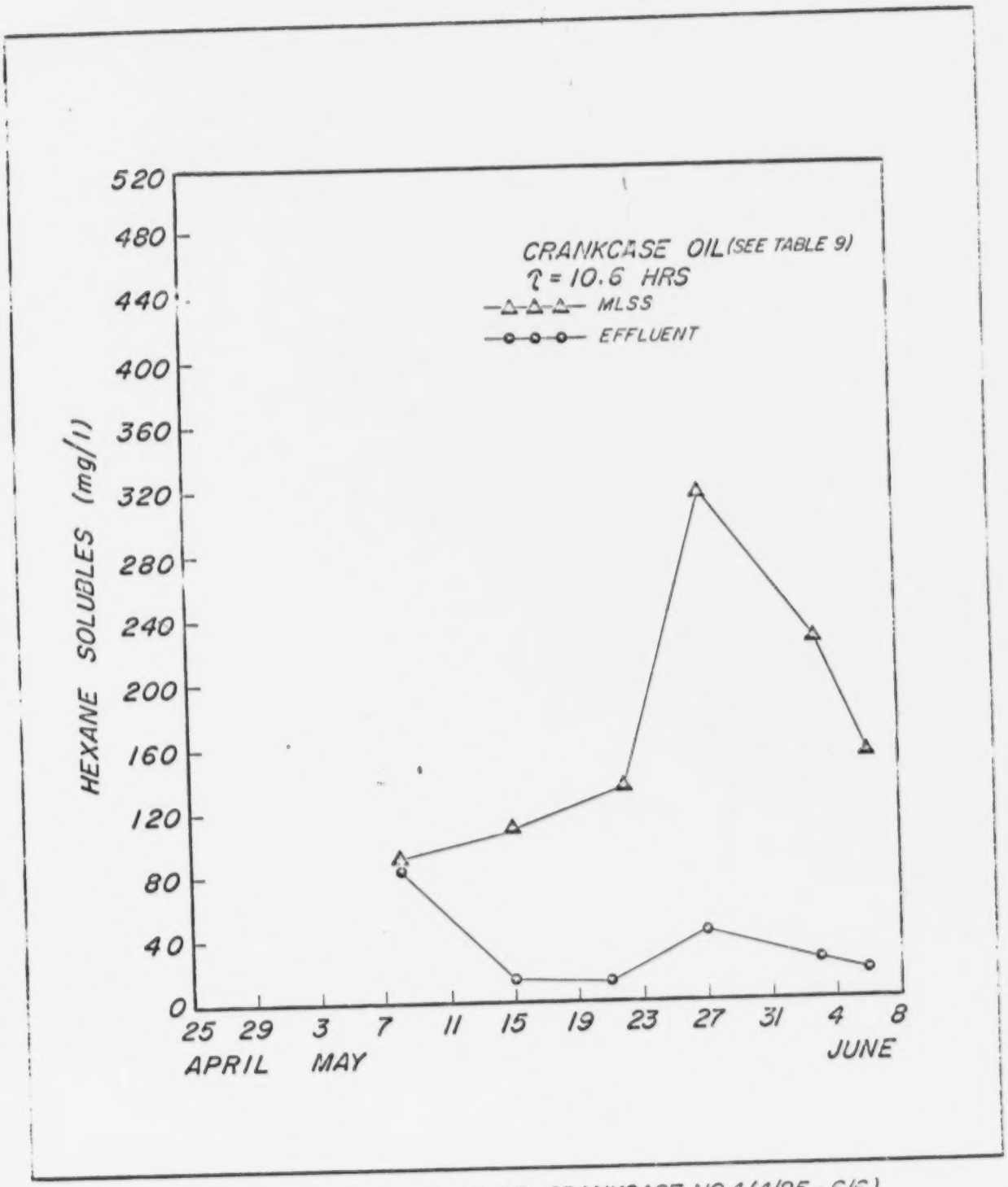
## Detention Time Studies

In the detention time studies, four units and a control were set up and operated treating crankcase oil. Three of the units operated at the same oil loading rates but at varying detention times, while the fourth unit operated at a higher loading level. The operating conditions and performance data from the study is presented in Table 9. The three units operating at the same loading rate show substantially the same behavior. Typical mixed liquor hexane content data and effluent suspended solids information is presented in Figures 16, 17, and 18. After an initial unsettled period, the systems settled down and provided an effluent of comparable quality to the control. Data showing the variation in the system at higher oil loading is presented in Figures 19 and 20. In this case, the system does not adjust

TABLE 9

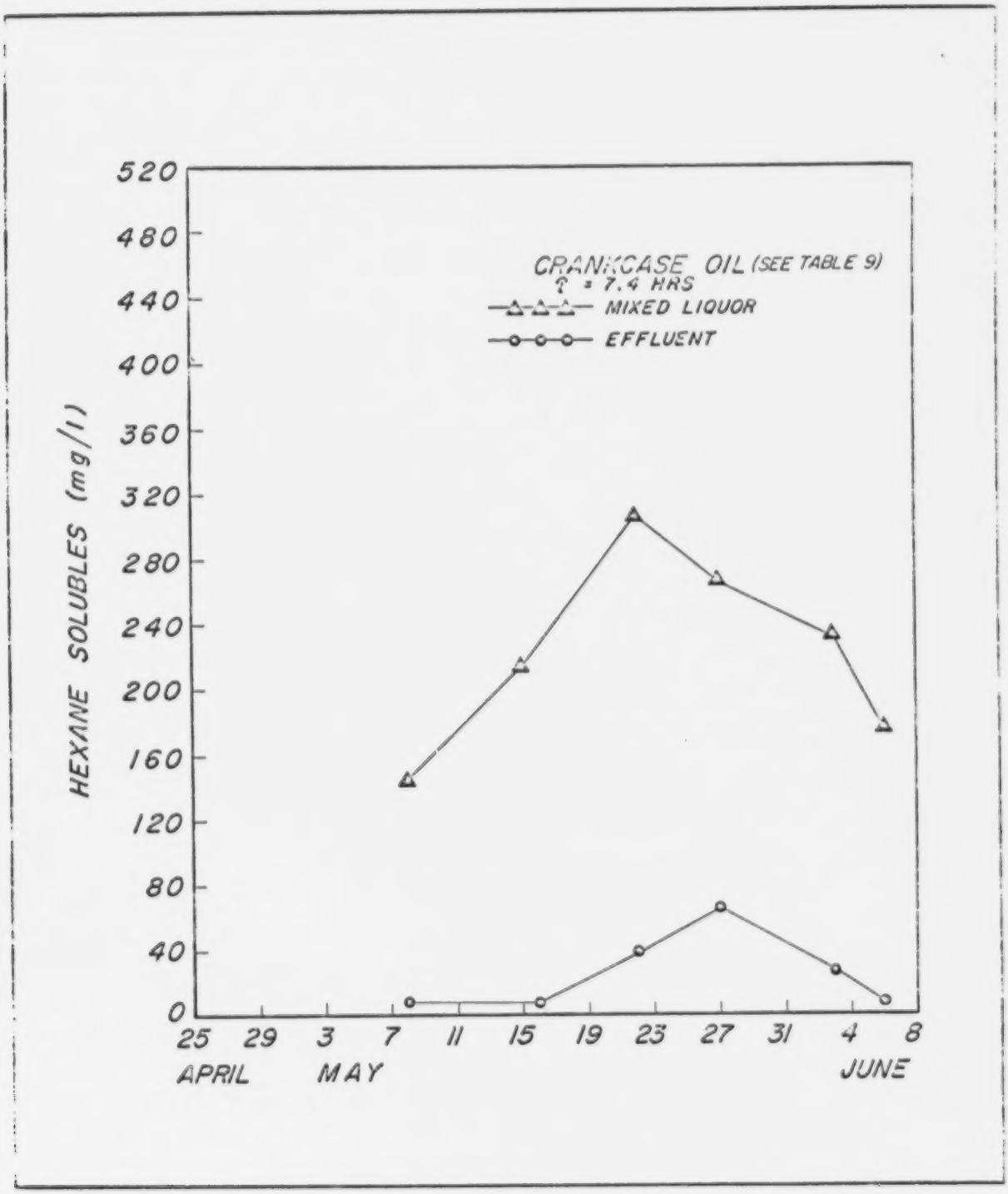
EFFECT OF DETENTION TIME ON SYSTEM PERFORMANCE
CRANKCASE OIL

| Detention Time (hours) | BOD in (mg/l) | COD in (mg/l) | Oil Added (mg/l | Hexane Solubles Recovered (mg/l) | MLSS (mg/l) | COD out (mg/l) | Effluent Suspended Solids (mg/l) | Loading Rate mg Oil / mg MLSS |
|---|---|---|---|---|---|---|---|---|
| Control 7.3 | 296 | 315 | | | 2,152 | 57 | 30 | |
| 7.4 | 296 | 315 | 34.9 | 28.6 | 1,928 | 69 | 40 | 0.06 |
| 10.4 | 296 | 315 | 53.5 | 44.0 | 2,093 | 44 | 31 | 0.061 |
| 15.0 | 296 | 315 | 65.9 | 54.0 | 1,826 | 64 | 38 | 0.058 |
| 6.4 | 296 | 315 | 60.5 | 49.5 | 2,068 | 150 | 95 | 0.11 |




TEMPORAL HEXANE PLOT - CRANKCASE, NO.4 (4/25 - 6/6)

FIGURE 16




TEMPORAL HEXANE PLOT-CRANKCASE (4/25-6/3)

FIGURE 17

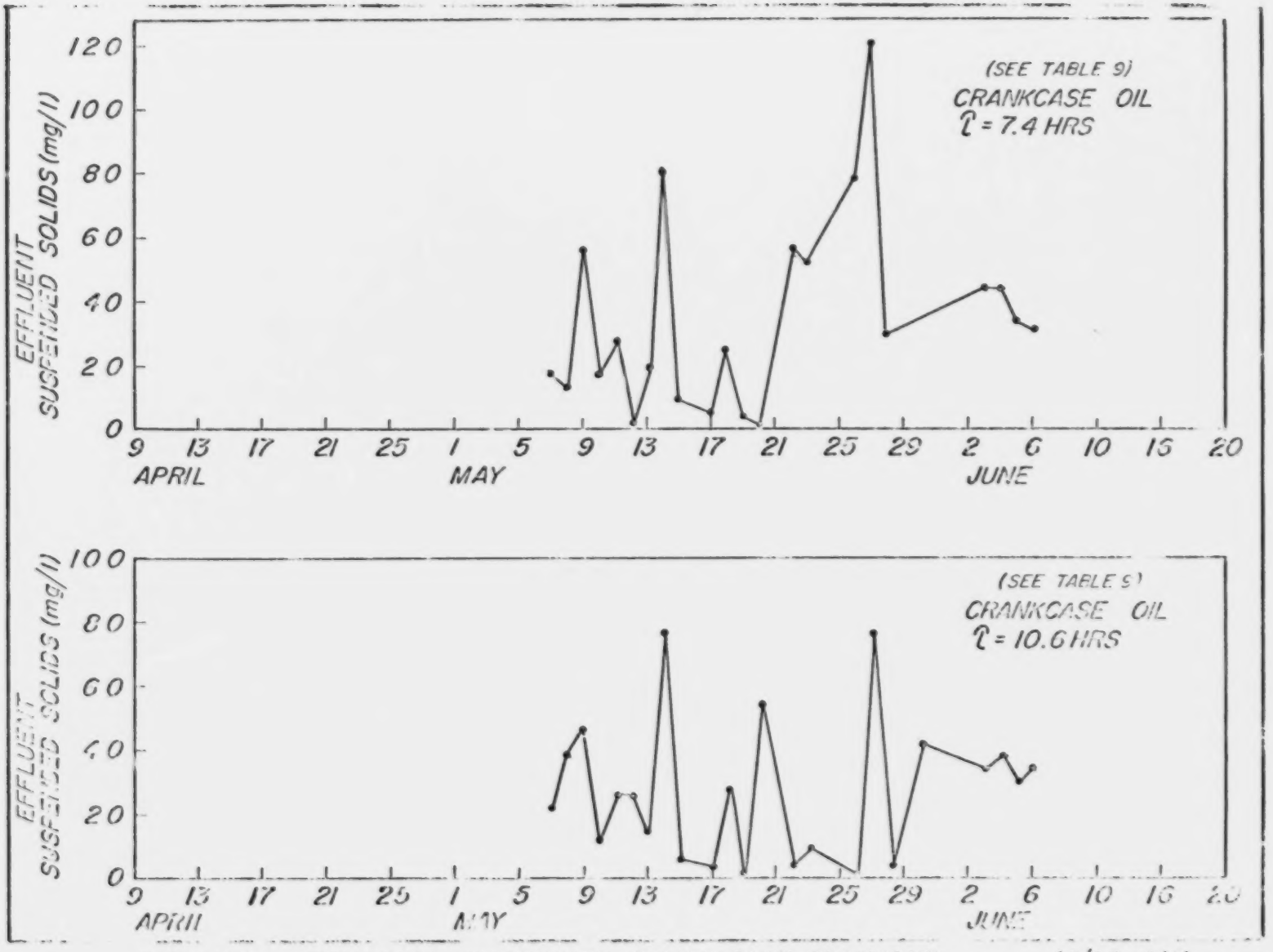
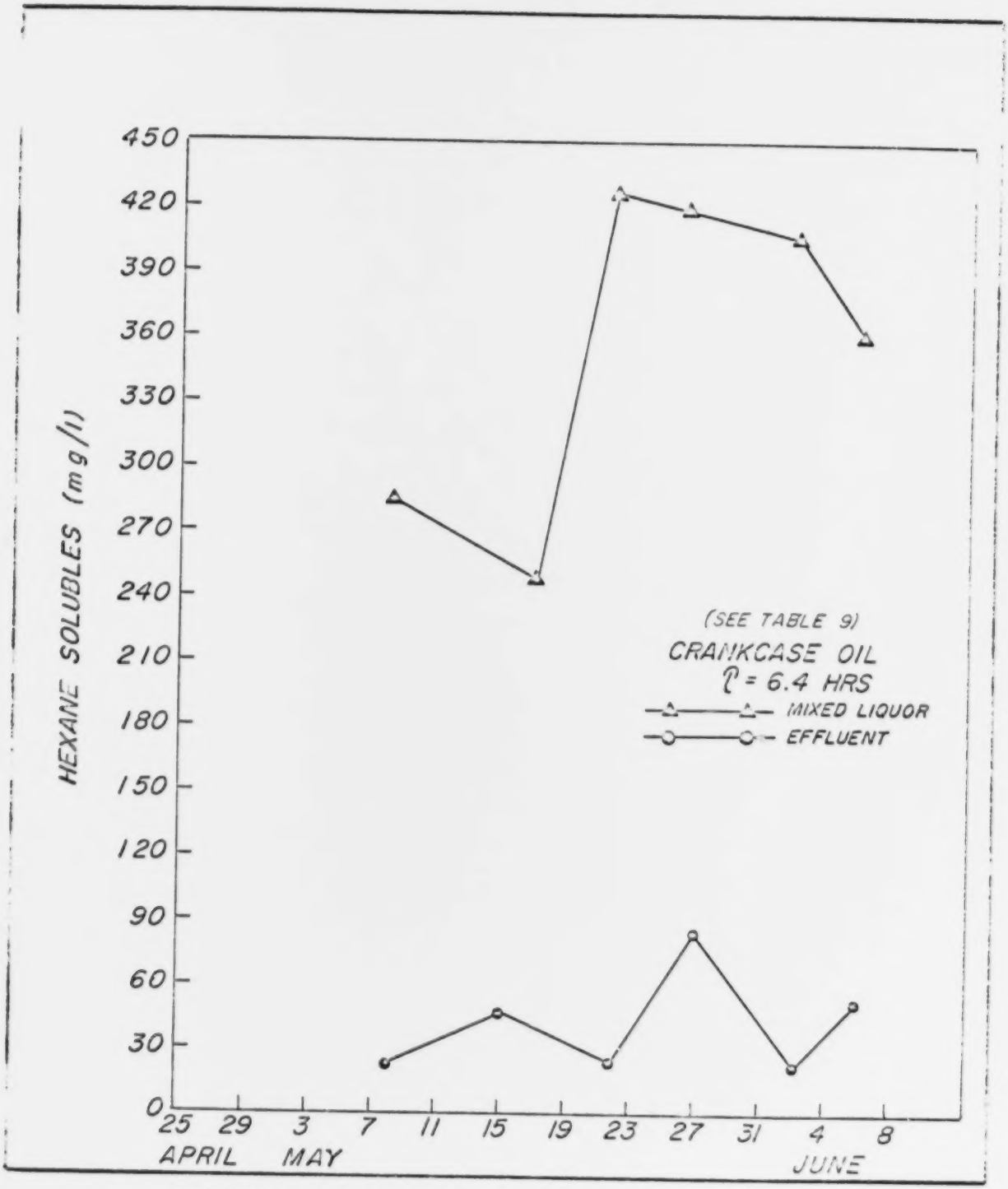



FIGURE 18- TEMPORAL SUSPENDED SOLIDS PLOT-CRANKCASE (4/25-6/6)




TEMPORAL HEXANE PLOT - CRANKCASE (4/25-6/6)

FIGURE 19

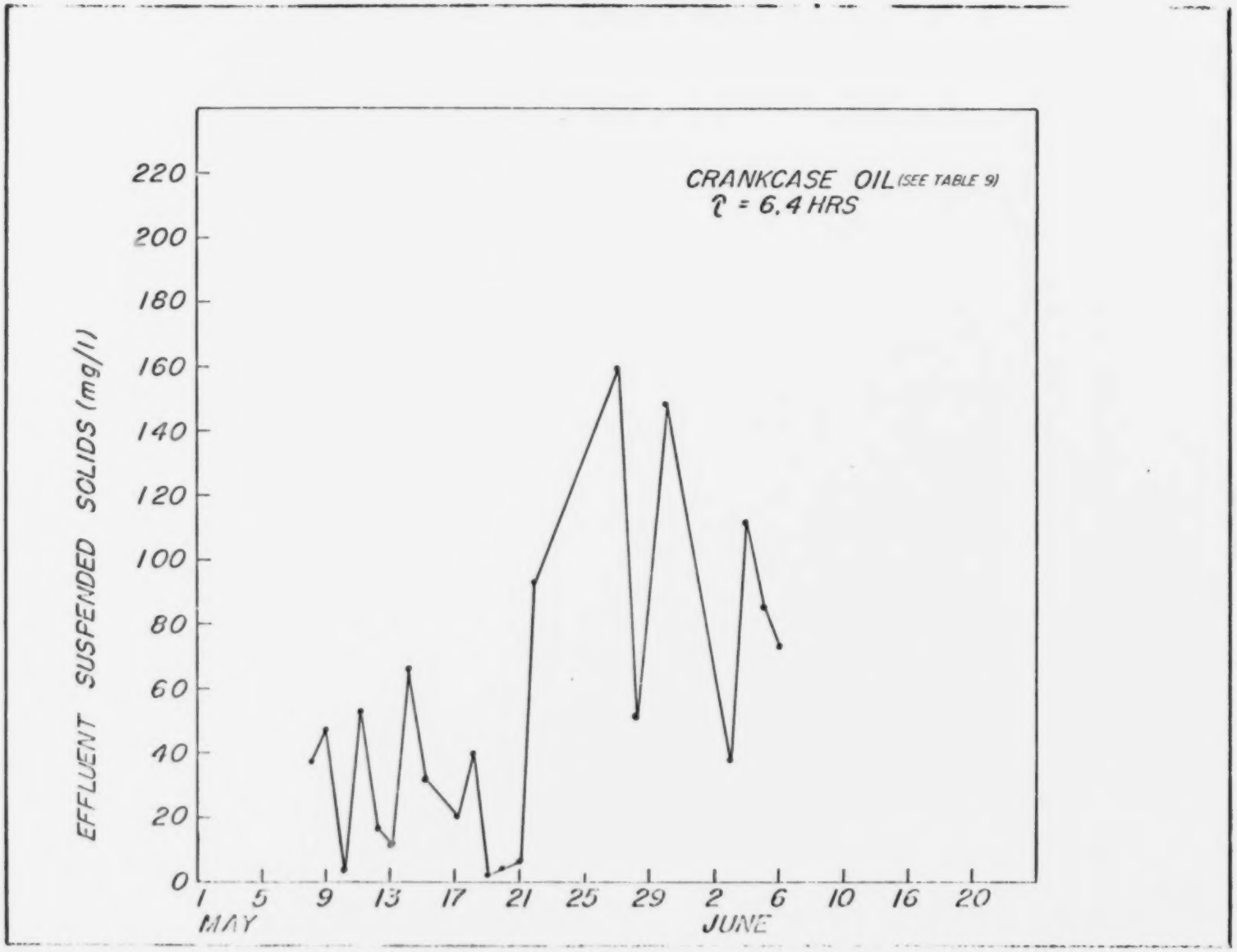



FIGURE 20 - TEMPORAL SUSPENDED SOLIDS- CRANKCASE (4/25-6/6)

but continues at an unacceptable level of solids loss even after acclimization. This study was continued significantly beyond the period of data collection to determine if later acclimization occurred, but it did not.

Perusing the test data, one may conclude that in the experiments, oil loading rate more directly controls system performance than does detention time. It should be pointed out, however, that this observation may have limitations. In practice, as the detention time increases, the new sludge cells produced per day decrease, and this phenomenon, not explored herein, may have some influence on the efficacy of the system with respect to oil removal.

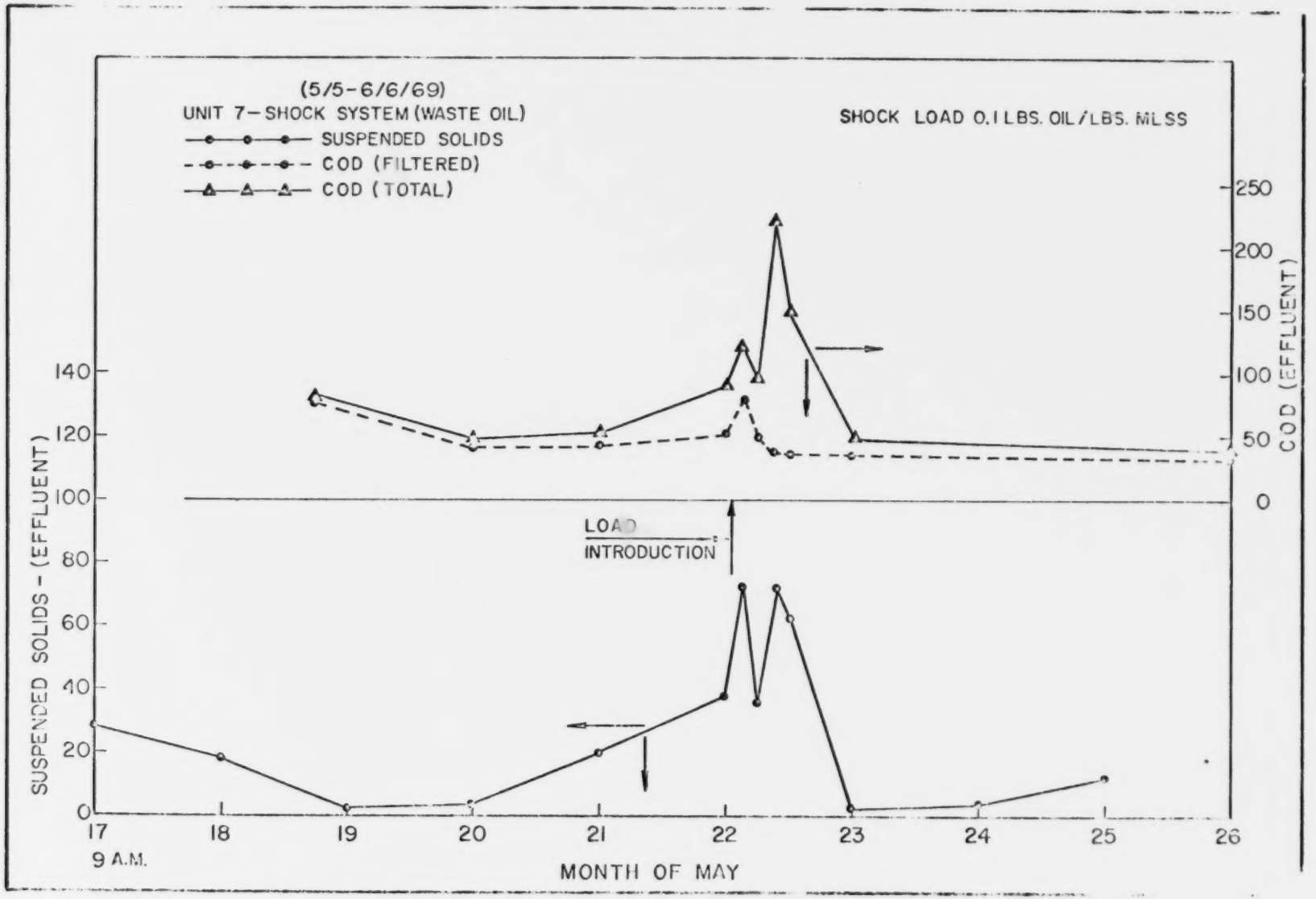
## Acclimatization To Crude Oil

An attempt was made to develop a culture that would utilize crude oil as its primary substrate. The system was stabilized as a mixture of synthetic sewage and oil for several weeks. After thorough acclimatization the sewage was gradually removed from the system. Despite all attempts to control losses the system solids deteriorated to a low level and a totally dispersed floc developed. All similarity to activated sludge was lost.

It was possible by filtering the organisms from the effluent to maintain a culture that did have an uptake rate and was capable of stabilizing the crude oil to some degree. Unfortunately, the analytical tools to measure these changes were not available. The experiment did demonstrate the possibility of developing a biological culture capable of utilizing crude oil as a primary substrate but the conditions for maintenance of optimum life appear to be substantially different from activated sludge.

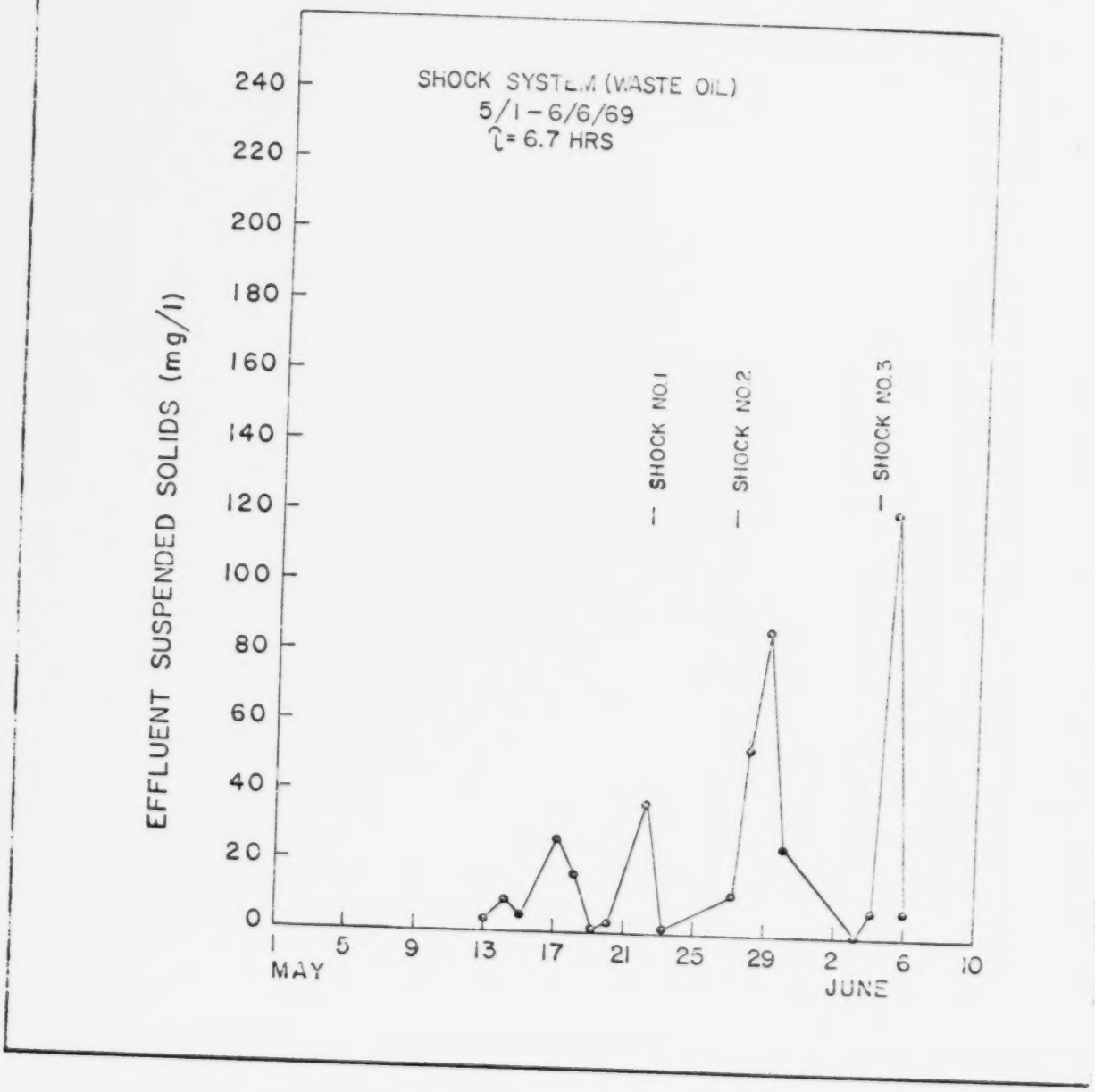
## Shock Loading Studies

To investigate system response to shock loading, standard systems were set up and operated on a synthetic sewage feed. At intervals, a shock load of the study substrate was introduced into the system. The results for the refinery waste oil typify the data obtained. Figure 21 shows the system response after a shock load equivalent to 0.1 pound of oil/pound mixed liquor suspended solids. As seen in Figure 21 immediately after the load was introduced, the suspended solids and COD of the effluent rose sharply, but the filtered COD shows little change. Within 24 hours the system has returned to normal operation. The system was rested 5 days, then was shocked again and then again after 10 days. The longer term data is presented in Figures 22, 23, and 24. In the first case, the



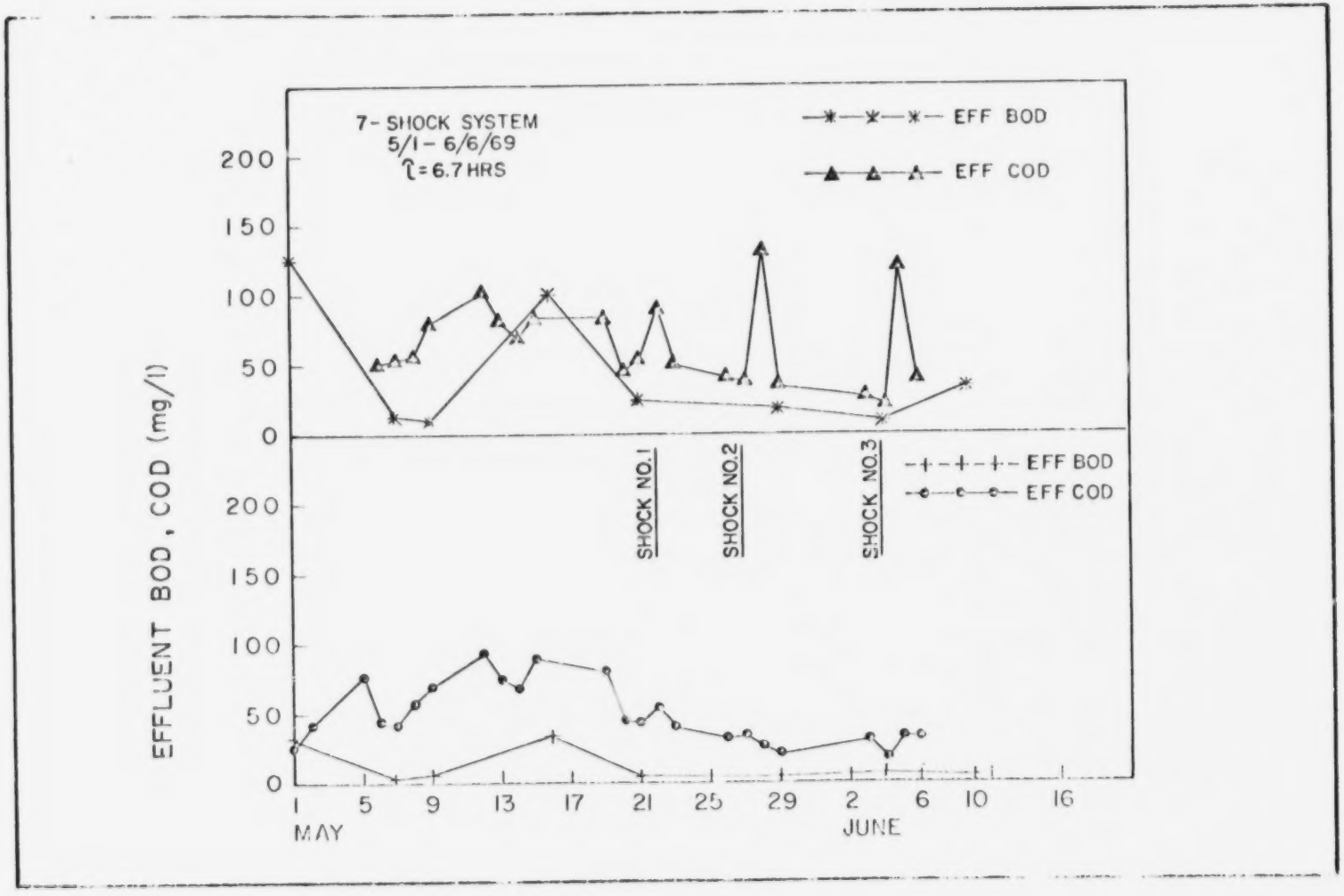

TEMPORAL COD & SS PLOT OF WASTE OIL SLUG, SHOCK NO. 1

FIGURE 21



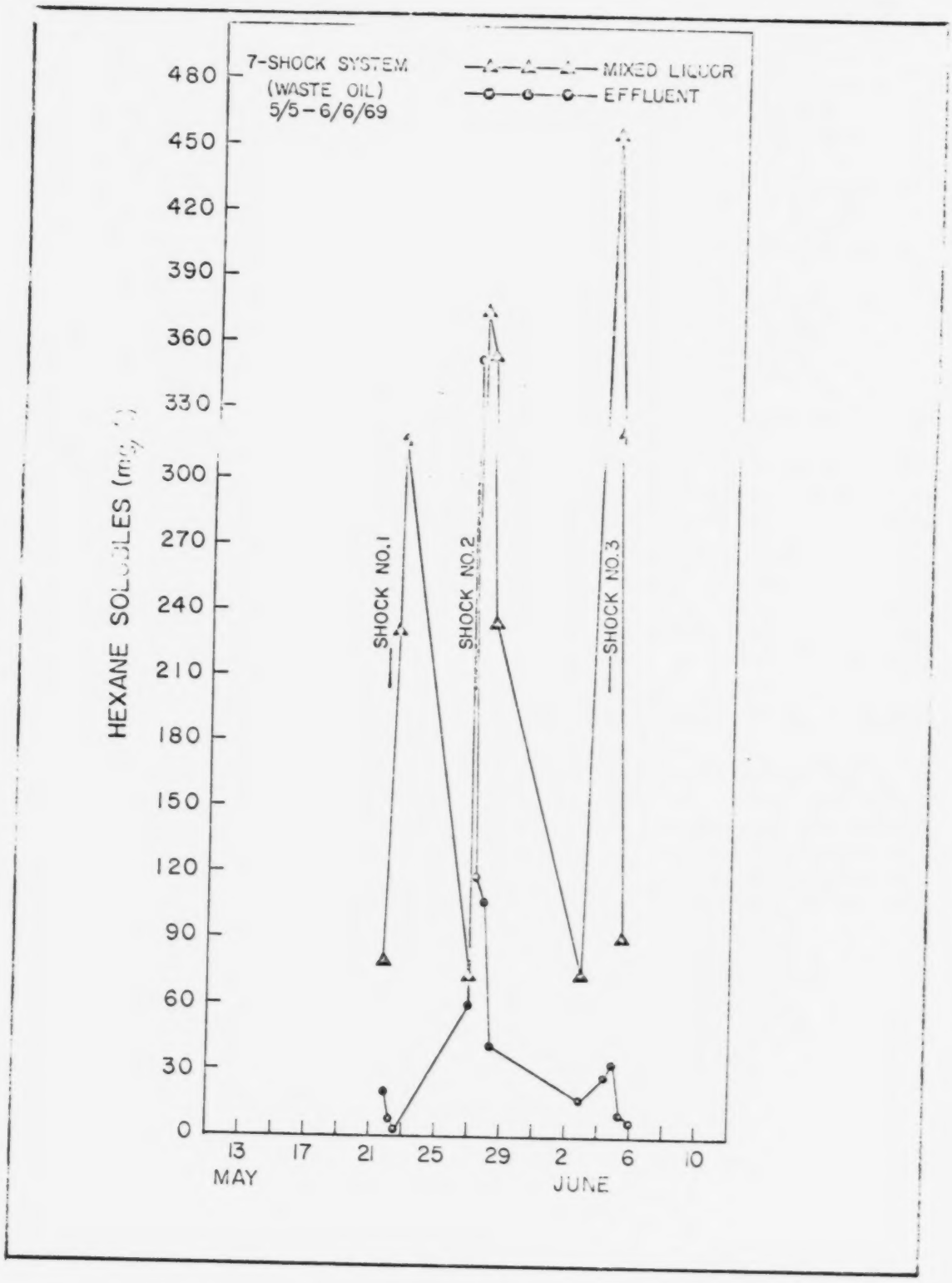

TEMPORAL SUSPENDED SOLIDS PLOT, WASTE OIL SHOCK STUDY

FIGURE 22




TEMPORAL BOD, COD PLOTS, WASTE OIL SHOCK STUDY

FIGURE 23




TEMPORAL HEXANE PLOT, WASTE OIL SHOCK STUDY

FIGURE 24

system absorbs virtually all of the test substrate, (refer to Figure 24), with almost none appearing in the effluent, except that associated with the lost suspended solids. In the second shock, the load was 0.5 pounds of oil per pound of mixed liquor suspended solids. In this case, the biological system was unable to adsorb the substrate and it is washed out in the effluent over the next 26 hours. The sludge increased to a maximum in hexane soluble content from which it gradually purged itself. The upset in the effluent suspended solids and COD is apparent for several days but the system does recover.

The third shock is equivalent to 0.10 pounds oil per pound mixed liquor as in the first case, but is introduced over 28 hours rather than as a point injection. In this case, the return of the sludge hexane soluble level is somewhat quicker than before, but all other responses are about the same as in the previous cases.

Examination of other study substrates produces essentially the same data. Although a detailed quantative evaluation is impossible, the qualitative assessment of the observations is consistent with the results obtained for the continuously fed system. The response is principally physical with the entrapped oil compound being very slowly degraded. Shock load, even very high loads, do not destroy the system but rather disrupt it for a short while until the density conditions necessary for proper balance return.

## Industrial Waste Studies

A brief investigation was conducted to determine if different reactions could be expected with a diverse basis substrate, mainly an industrial waste rather than sewage. Relatively little quantative data was obtained and the study was discontinued when it became apparent that the response of the system was quite similar to that recounted for the sewage system.

## GENERAL DISCUSSION OF TEST DATA

The data and observations gathered during the study defined a most confusing situation. The ability to clearly handle the information is further restricted by the limited validity of certain of the measurements and the inability to define the nature of changes occuring in the test substrates. It is possible, however, to draw certain conclusions from the data and observations.

### Biological Considerations

The oil compounds do not exhibit toxic or inhibiting effects on the biological culture. This observation is confirmed by continued high levels of organic removal of the systems even until conditions of obvious physical failure, and from detailed microscopic studies conducted continuously throughout the studies. The presence in virtually all units of free swimming and stalked ciliates, as well as a significant rotifer population, indicated healthy microbial conditions existed in each of the systems.

Correlary with the lack of biological inhibition is the surmise that the oil compounds collect in the floc and outside the cell wall.

The oily materials are each biodegraded to some extent. Observations indicate however, that even after substantial times, significant residue persists. Unfortunately, it was not possible to determine the nature of the residue in the present experiments.

Evidence is available indicating that activated sludge will very effectively adsorb the oily compounds with which it comes in contact. The sludge will then proceed to oxidize the compound but at a very slow rate. The period of acclimation of the sludge to the test compounds was quite long, the average period being about two weeks.

### Oxygen Transfer Studies

Studies were initiated to determine if the test compounds influenced the transfer of oxygen to the system. No noticeable effect was identified. This observation is consistent with the previously stated conclusion that the substrates are adsorbed onto the biological floc very quickly. The material thus adsorbed is not free to concentrate at an oxygen transfer interface and cause degradation of system efficiency.

## Sludge Settling Characteristics

The studies have clearly shown that inoperability of a conventional activated sludge system occurred as a result of a destruction of the settling properties of the floc. Under such conditions the loss of solids from the system was greater than the buildup and continued deterioration occurred.

The settling phenomena associated with activated sludge is somewhat poorly defined. Experiments have indicated that most well settling sludges have a density of about 1.016. If the density of the floc is reduced to about 1.008 or less, random turbulence is usually sufficient to maintain the cells in suspension and the settling is greviously impaired.

In the case where activated sludge is contacted with an oil compound that is adsorbed but not biologically assimilated, the resulting density for any combination of sludge and oil can be calculated. This calculation has been performed and is presented in Table 10. It will be noted from the Table that for any system, undesirable settling properties may be expected to develop when the oil content approaches 5% of the mixed liquor suspended solids in the system. (Based on the 2,000 to 3,000 mg/l study range this is a sludge oil content of 100 to 150 mg/l.) This calculation relates only to the unacclimated system, such as the batch case. In the continuous system, a certain fraction of the oil material is metabolized by the bacterial system and although complete oxidation does not occur, some change resulting in an apparent increase in density occurs. The continuous, acclimated system is therefore able to operate satisfactorily at somewhat higher mixed liquor oil levels.

TABLE 10

CALCULATED DENSITIES OF OIL-ACTIVATED SLUDGE MIXTURE

| # | System | Density at indicated percent Hexane Extractables | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 100 | 1.25 | 2.5 | 5.0 | 12.5 | 25.0 |
| A | Activated Sludge | 1.016 | | | | | | |
| B | Crankcase | 1.00 | 0.899 | 1.013 | 1.0116 | 1.010 | 1.003 | .986 |
| C | Crude Oil | 1.00 | 0.846 | 1.0125 | 1.010 | 1.007 | .996 | .974 |
| D | Waste Oil | 1.00 | 0.840 | 1.0120 | 1.010 | 1.007 | .995 | .972 |
| E | Vegetable | 1.00 | 0.909 | 1.013 | 1.0116 | 1.010 | 1.003 | .989 |

Example:
At 5.0% under Crankcase oil (B) implies a system with activated sludge at a concentration of 2,000 mg/l and a crankcase concentration of 25 mg/l.

Note:
Unacceptable settling properties develop below 1.008.

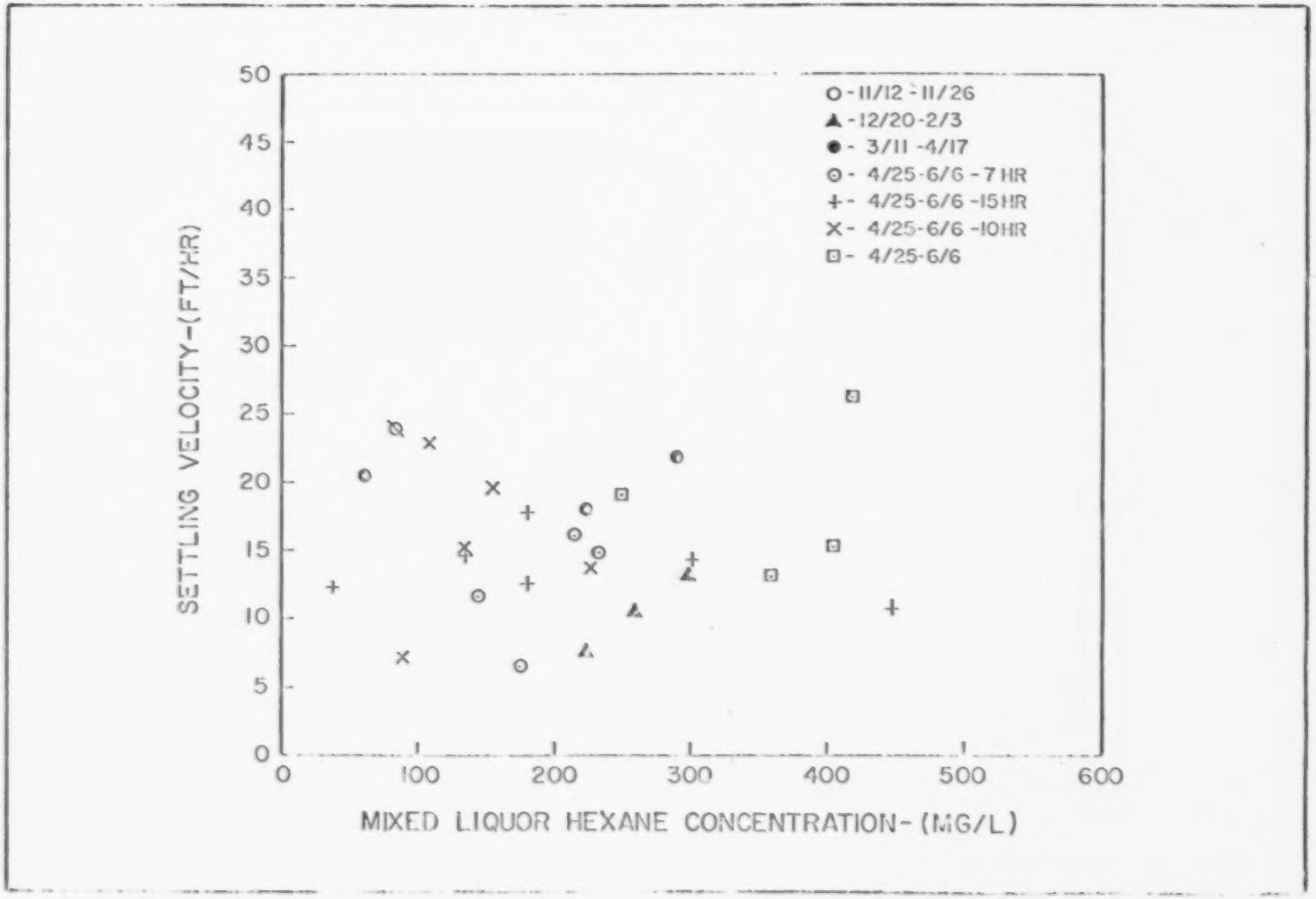
## Study Measurements

Related efforts to develop a suitable method for measurement of sludge density were not successful, and it was therefore necessary to use sludge settling rate as a primary measurement. Each of the study systems were investigated twice a week for settling rate and sludge oil content. A typical correlation of the data is presented in Figure 25. Although a variety of correlation techniques have been employed, it is not possible to relate the settling velocity to the sludge oil content. A trend of decreasing velocity with increasing oil content is generally observed but the data is not sufficiently defined to quantatively identify the tendency. For crankcase oil and vegetable oil, it has been possible to relate a portion of the effluent suspended solids loss data to oil loading. This correlation is shown in Figure 26. A similar correlation cannot be drawn for the other test substrates due to the limited range of loading data. Examination of all available data indicates that a loading range of from 0.075 to 0.10 pounds oil/pounds sludge is the range of loading in which settling problems begin to develop.

## Efficiency of Removal of Hexane Soluble Materials

Although not of prime concern, it is germane to consider the efficiency of the biological system with respect to oil removal. A detailed examination of the data indicates that all measurable hexane soluble materials in the effluent were associated with suspended solids carryover. If the suspended solids were filtered out, the hexane solubles remaining in the effluent approached zero.

It should be noted that the test systems had a submerged discharge from the aeration tank and that in a system where this is not the case some floating hexane soluble materials may enter the final clarifier or receiving water.




SETTLING VELOCITY VS. MIXED LIQUOR HEXANE CONCENTRATION-(MG/L)

FIGURE 25

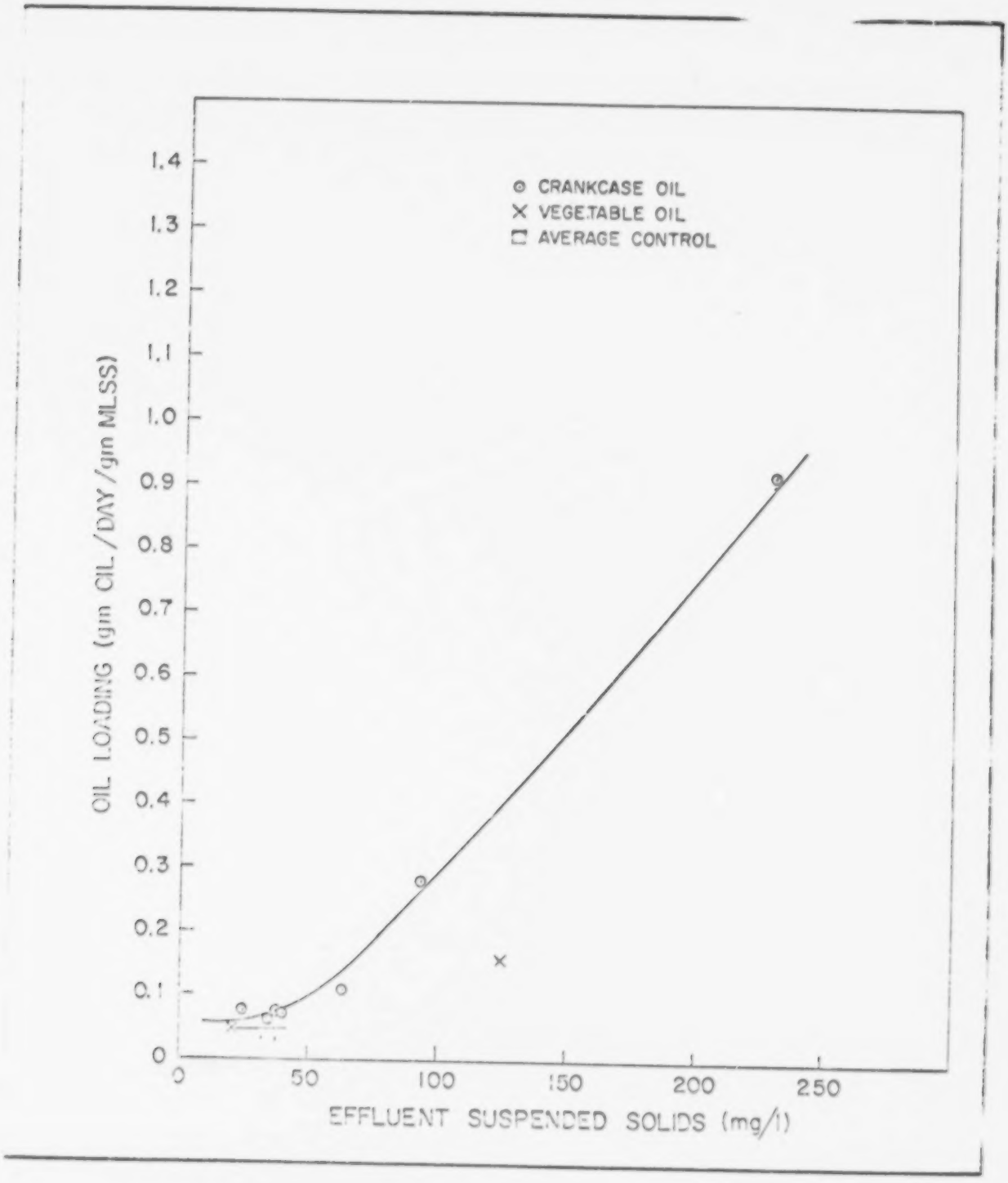

CRANKCASE OIL
VEGETABLE OIL
AVERAGE CONTROL
OIL LOADING (gm OIL/DAY/gm MLSS)
EFFLUENT SUSPENDED SOLIDS (mg/l)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
50
100
150
200
250

FIGURE 26

## SUMMARY

The failure of activated sludge system due to oily materials is physical rather than biochemical. The oily compounds are adsorbed in the sludge floc but are only slowly assimilated. The results of accumulation of oil in the floc is a lowering of density which results in a loss of culture settling properties. Once the culture settling properties have been impaired to the point where the solids loss is greater than the rate of sludge buildup, a system failure occurs.

STUDY SECTION TWO

# REMOVAL OF OILY COMPOUNDS BEFORE BIOLOGICAL TREATMENT

In view of the difficulties associated with biological treatment of various insoluble hydrocarbons it appears germane to explore pretreatment steps that might be employed to prohibit such materials from entering the biological system in the first place. Consistent with the project objectives, those processes and unit operations compatible with conventional biological treatment have been given most significant attention. Both physical and chemical systems have been studied and included coagulation, adsorption, flocculation, and filtration.

## Coagulation And Adsorption

### Theory And Practice

### Coagulation

Coagulation is employed for the removal of waste materials in suspended or colloidal form. Colloids are represented by particles over a size range of $10^{-5}$ cm to $10^{-7}$ cm. These particles do not settle out on standing and cannot be removed by conventional physical treatment processes. Mixtures involving the dispersion of one liquid in another are known as emulsions.

Colloidal systems possess electrical properties which create a repelling force and prevent agglomeration and settling. Colloids can be either hydrophobic or hydrophilic. The hydrophobic colloids possess no affinity for the liquid medium and lack stability in the presence of electrolytes. They are readily susceptible to coagulation. Hydrophilic colloids exhibit a marked affinity for water. The absorbed water retards flocculation and frequently requires special treatment to achieve effective coagulation.

The stability of a colloid is due primarily to electrostatic forces and neutralization of this charge is necessary to induce flocculation and precipitation. The vast majority of colloids in wastes possess a negative charge, so coagulation can usually be induced by the addition of high valence cations. Coagulation results from two basic mechanisms: perikinetic or electrokinetic coagulation, in which the electrostatic forces are reduced by ions or colloids of opposite charge to a level below the van der Wells attractive force; and orthokinetic coagulation, in which the micelles aggregate and form clumps which agglomerate the colloidal particles.

The addition of high valence cations disperses the particle charge. As the coagulant dissolves, the cations serve to neutralize the negative charge on the colloids. Microflocs are formed which retain a positive charge in the acid range because

of the adsorption of hydrogen ions. These microflocs also serve to neutralize and coat the colloidal particles. Flocculation agglomerates the colloids. In this phase, surface adsorption is also active. Colloids not initially adsorbed are removed by enmeshment in the floc.

A polyelectrolyte is generally regarded as a coagulant aid, but can serve as a coagulant itself by reducing the effective charge on a colloid. Polyelectrolytes are high molecular weight polymers which contain adsorbable groups and form bridges between particles or charged flocs. There are three (3) types of polyelectrolytes: a cationic, which adsorbs on a negative colloid or floc particle; an anionic, which replaces the anionic groups on a colloidal particle and permits hydrogen bonding between the colloid and the polymer; and a nonionic, which adsorbs the flocculates by hydrogen bonding between the solid surfaces and the polar groups in the polymer.

This study examined two of the most common coagulants in waste treatment application, aluminum sulfate or alum, and ferric chloride. Aluminum hydroxide is amphoteric in that it can act as either an acid or a base. Under acidic conditions it has the following properties:

$$(Al^{+3})(6H^{-3}) = 1.9 \times 10^{-3}$$

(pH = 4, 51.3 mg/l $Al^{-3}$ is in solution.) And under alkaline conditions:

$$(AlO^{-})(H^{+}) = 4 \times 10^{-13}$$

(pH = 9, 10.8 mg/l of aluminum is in solution.) The ferric ion has the following properties:

$$(Fe^{+3})(OH)^{3} = 10^{-36}$$

(Insoluble hydrous ferric oxide is produced for a pH range of 3.0 to 13.0.)

Adsorption

Organic material in a waste can frequently be removed by adsorption on an active solid surface. A solution in contact with a solid surface has the tendency to condense upon that surface. This phenomenon is defined as adsorption.

Removal of pollutants from a solution in an adsorption process is dependent on both chemical and physical properties. Chemical adsorption results in the formation of a mono-molecular layer of the pollutant on the surface of the adsorbent, due to forces of residual valence of the surface molecule.

Physical adsorption results from molecular condensation in the capillaries of the porous adsorbent. In general, substances of highest molecular weight are most easily adsorbed. Chemical adsorption is rapid in that an equilibrium concentration of the pollutant forms on the interfacial surface of the adsorbent, while diffusion into the adsorbent particles is slow. The overall rate of adsorption is controlled by the rate of diffusion of the solute molecules within the capillary pores.

The adsorptive capacity of an adsorbent is dependent on the characteristics of both the adsorbent and the waste. The rate of adsorption varies inversely with the particle diameter of the adsorbent, increases with increasing concentration of solute, increases with increasing temperature and increases with decreasing pH due to the surface charges of the adsorbent. In addition, the rate of adsorption varies with the time of contact with the waste.

Activated carbon is the most commonly used adsorbent. In addition to activated carbon, an evaluation of bentonite and diatomaceous earth as adsorbents for use in removing the hexane soluble oils was performed.

In these studies only fresh powder carbon was used and no attempt was made to determine the regenerative capacity of the carbon. The large quantity of carbon required to effect the necessary removals of the hexane solubles in the waste economically requires the reuse of the carbon for this to be a feasible treatment alternative. Further studies would be required to determine (a) the loss of carbon from a treatment system, and (b) the effect the waste characteristics would have on the adsorptive capacity of the carbon regenerated for reuse.

Activated carbon can be reactivated for reuse by several methods. Some of these methods are:

1. controlled incineration of the spent carbon;

2. caustic or acid wash of the spent materials;

3. solvent extraction to remove the adsorbed material from the carbon;

4. use of superheated steam.

The most common method of carbon regeneration, however, is thermal reactivation. The spent carbon is dewatered and fed to a furnace where the adsorbed organic contaminants are burned from the carbon.

Bentonite is composed mainly of the clay material montmorillonite. Pure clay is a mass of mineral fragments, strongly bound together when dry, but separable, — when dispersed in water, — into myriads of particles, many of which are microscopic in size.

The montmorillonite or bentonite clays may be divided into two general classes: (1) those that absorb large quantities of water, "swelling" enormously in the process, and that have the property of remaining in suspension in their water dispersions; (2) those that absorb only slightly more water than ordinary plastic clays or fullerr's earths, do not swell noticeably, and settle rapidly in this water dispersion. Type 1 is known as "sodium bentonite", and type 2 is "calcium bentonite". The dominance of either lime or soda is an important factor in causing swelling or non-swelling.

The two properties of adsorption and electrokinetic behavior are the major mechanisms which enable montmorillonite clays to effect an emulsion break and clarification in treating process wastes.

The procedure followed in the adsorption studies was as follows:

1. the waste samples were mixed with various dosages of adsorbent;

2. the adsorbent was filtered from the mixture and the hexane soluble concentration remaining in solution was measured.

Experimental Results

A series of experiments were set up to examine the removal of oil materials from a domestic influent to which chemical and adsorptive materials were added to an oil-sewage mixture. The concentration of oil studied ranged from 100 to 215 mg/l in the mixed system. The overall results from the experiments demonstrated that dosages in the range of 1 gram chemical per gram oil present reduced the effluent hexane extractables level to less than 30 mg/l. Based on the results from the biological units, oil entering a biological system at this level would have a minor effect on the performance of the plant. Two typical experiments are presentd in which crude oil and crankcase oil were the test materials.

Crankcase oil and crude oil were added to separate units containing a raw waste from a local treatment plant. This mixture was supplemented with an anionic emulsifier in order to

provide an emulsified system. Before settling, the hexane level of crankcase oil and crude oil was 105 and 211 mg/l, respectively. The mixture was then settled for two hours and the supernatant examined for oil remaining. A settling period was imposed to simulate treatment in a primary clarification unit or separate pretreatment device. The additives studied were alum, ferric chloride, activated carbon, bentonite, and diatomaceous earth. The jar test procedure was used as the testing method, and is described in the Appendix. The supernatent from the adsorption study was filtered through a coarse media before analyzing for hexane soluble materials.

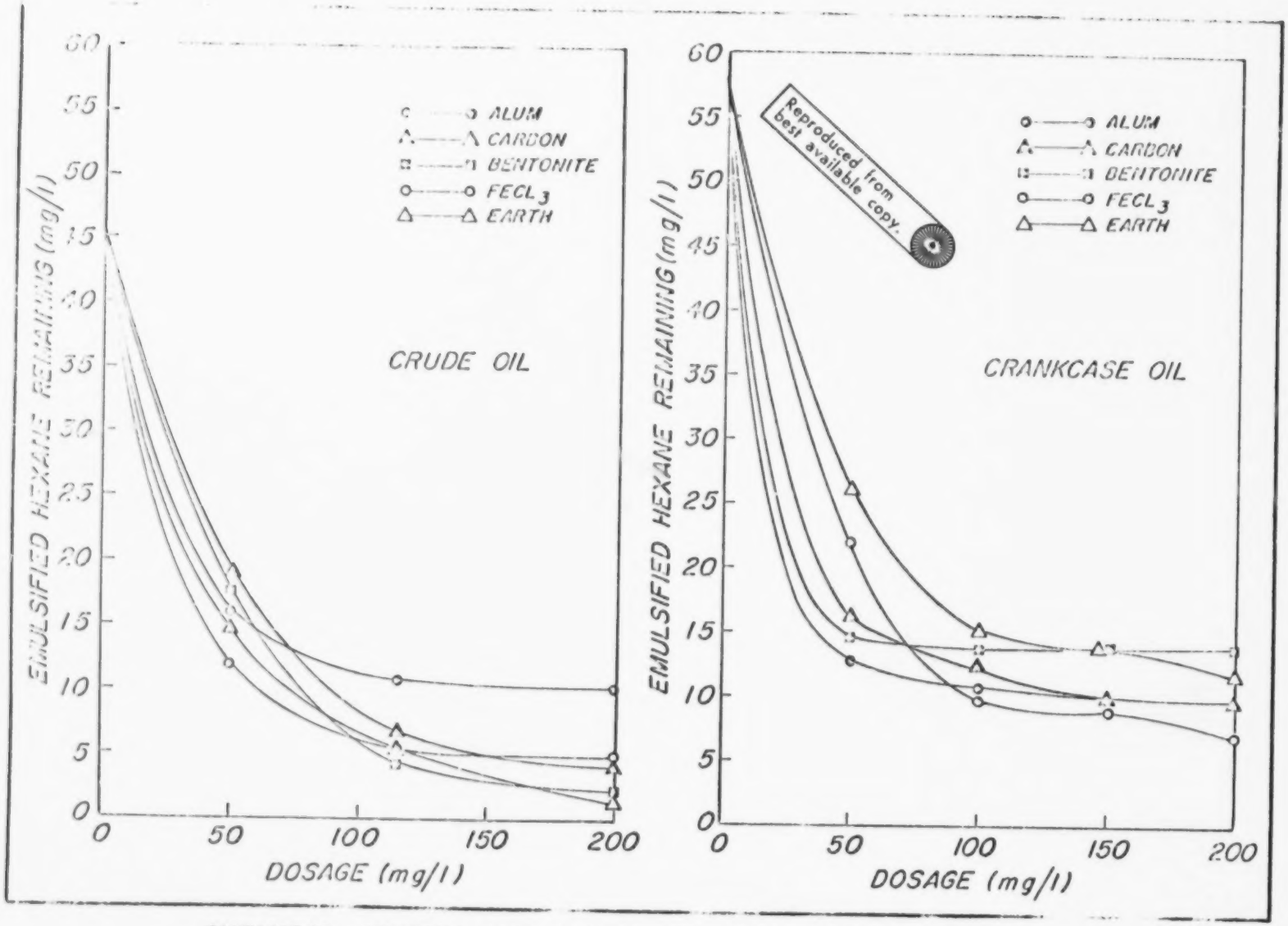
The results for the two test materials are presented on Figure 27. In either case system, any of the additives or dosages of 100 mg/l reduced the oil level to less than 15 mg/l. Dosages of only 50 mg/l were required to have effluent oil level less than 30 mg/l. The results obtained with the study of vegetable oil and crude oil are even more drastic: these materials reduced below problem levels with 25 to 50 mg/l of any addition. Further studies showed that for the range of emulsifants usually encountered in sewage that the chemical dosage and effluent concentration of oils is independent of initial oil concentration. The process appears to be two phased, initial removal down to some level occuring easily and with minimal aid, while the second phase of removal requires chemical assistance.

In the case of any chemical addition, considerable sludge problems are created, the magnitude of the problem varying with the volume of material being handled.

The coagulation and adsorption studies demonstrated that this pretreatment operation could be used to eliminate major upsets in biological systems. In application, careful consideration should be given to the type of pretreatment system based on efficiency and economics of the operation and the sludge removal and handling ease.

## Flotation

The previous experiments suggest that in many cases, a simpler method of separation might be adequate. The least complicated method of separating an oil-water solution is providing a system where separation occurs through the action of gravity forces. The oil, being lighter than the water, will rise to the surface forming a film or layer over the surface. The separation can be achieved by gravity alone, if sufficient time is provided and if the concentration of emulsifying agents is sufficiently low. Since the time required for gravity separation is usually too long for conventional application, the process may be aided by aeration or dissolved air flotation.




CHEMICAL STUDIES FOR CRUDE OIL AND CRANKCASE OIL
FIGURE 27

## Theory

Flotation is used for the removal of suspended solids, oils, and greases from wastes as well as for the separation and concentration of sludges. In the process waste flow a portion of clarified effluent is pressurized to 40 to 60 psi in the presence of sufficient air to approach saturation. When the pressurized air-liquid mixture is reduced to atmospheric pressure in the flotation unit, minute air bubbles are released from solution. The oil and suspended solids are floated by these minute bubbles, which attach themselves to and become enmeshed in the floc particles. The air-solids mixture rises to the surface, where it is skimmed off. The clarified liquid is removed from the bottom of the flotation unit or through an underflow weir. When flocculent sludges are to be clarified, pressurized recycle will usually yield a superior effluent quality since the flocs are not subjected to shearing stresses through the pumps and pressurizing system, while primary system pressurization of the influent is most common.

The performance of a flotation system depends upon having sufficient air bubbles present to float substantially all of the test materials. An insufficient quantity of air will result in only partial flotation of the oils, and excessive air will yield no improvement. The performance of a flotation unit in terms of effluent quality and solids concentration in the float can be related to an air-solids ratio, which is usually defined as pounds of air released per pound of solids in the influent waste. Since these studies were concerned primarily with the removal of oil materials, the basic flotation relationship (given in the Appendix) was modified such that the effluent oil level leaving the flotation unit was a function of the air to influent oil concentration. The relationship used was:

$$\frac{A}{H_i} = \frac{1.3 S_a R(fP - 1)}{H_i}$$

where:

$H_i$ = influent oil concentration (mg/l)

$A$ = air available for reaction (mg/l)

$S_a$ = saturation value of air in water $cm^3/l$

$R$ = pressurized volume liters

$P$ = absolute pressure (psi)

$f$ = saturation achieved

The primary variables for flotation design are pressure, recycle ratio, influent oil concentration, retention period, and rise rate. The effluent oil level decreases and the concentration in the float increases with increasing retention period. When the flotation process is used primarily for clarification, a detention period of 20 to 30 minutes is adequate for separation and concentration. Rise rates of 1.5 to 4.0 gpm/square foot are commonly employed. When the process is employed for thickening, longer retention periods are necessary to permit the sludge to compact.

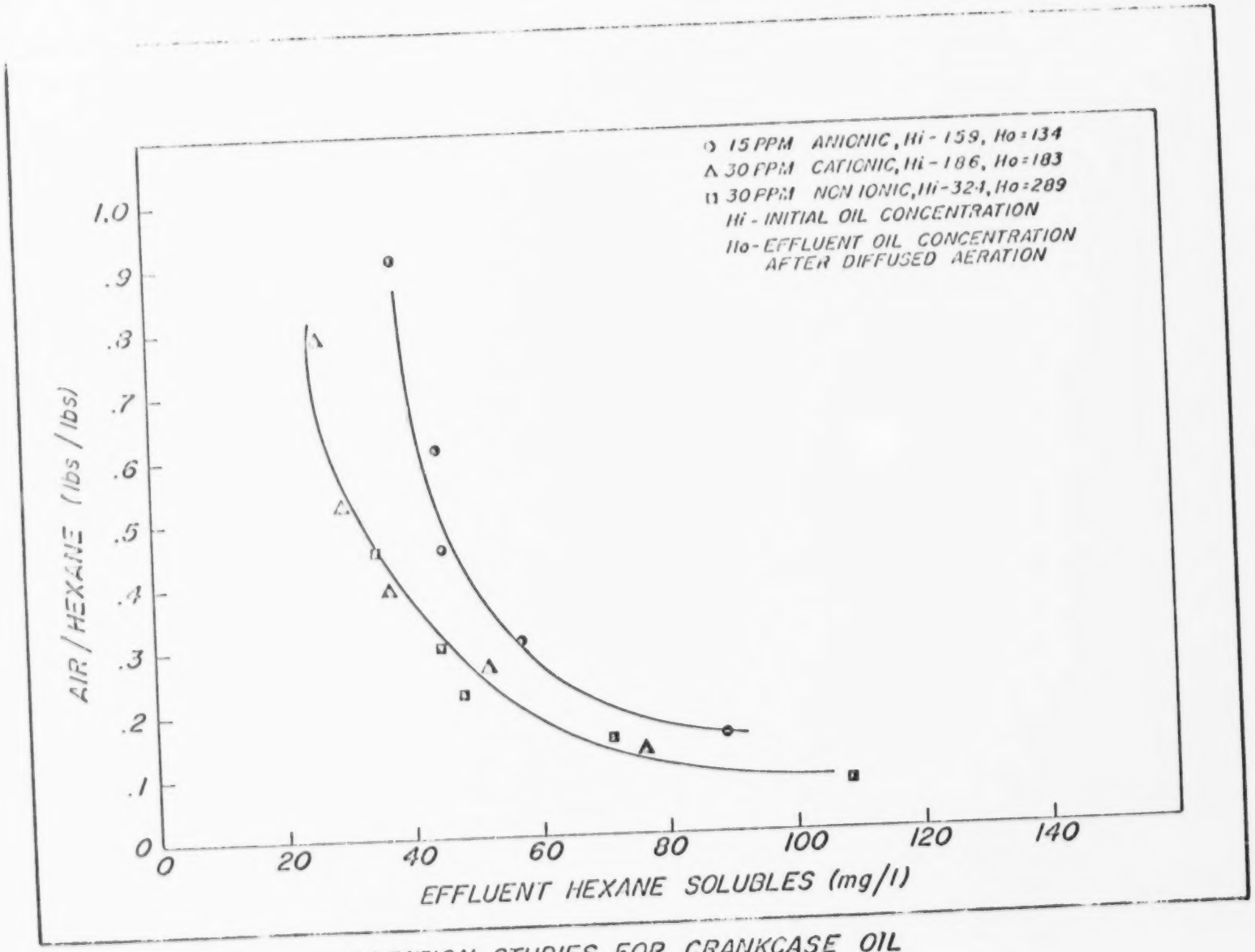
The principal components of a flotation system are a pressurizing pump, air injection facilities, a retention tank, a back pressure regulating device, and a flotation unit. The pressurizing pump creates an elevated pressure to increase the solubility of air. Air is usually added through an injector on the suction side of the pump, or under pressure on the downstream side. Of the total air induced, 30 to 45 percent will usually be dissolved.

The air and liquid are mixed under pressure in a retention tank with a detention time of one to three minutes. A back pressure regulating device maintains a constant head on the pressurizing pump. Various types of valves are used for this purpose. The flotation unit may be either circular or rectangluar with a skimming device to remove the thickened, floated sludge.

## Experimental Results

The initial phase of the flotation experiments consisted of the removal achieved by employing only diffused air for twenty minutes simulating the behavior of an aerated grit chamber. The experiments indicated that such a procedure would work acceptably and reduce the hexane soluble material to less than 30 mg/l, in a system containing no emulsifiers. In cases where emulsifiers were present more elaborate systems would be required.

In the main experiments the test materials were crankcase oil and refinery waste oil, mixed in a domestic influent that had been supplemented with an emulsifying agent. The emulsifiers added were an anionic compound, a cationic material, and a nonionic compound. The mixture, stirred overnight, was then tested using the flotation procedure given in the Appendix. A schematic of the apparatus is also presented in the Appendix. Basically, the study involved measuring the effluent oil content for different values of the air to hexane ratio. A typical output for crankcase oil is shown in Figure 28. The initial oil concentration ($H_i$) for the three emulsifier experiments are given on this Figure.




FLOTATION STUDIES FOR CRANKCASE OIL

FIGURE 28

Data is also presented for the concentrations of substrate remaining after diffused aeration, representing the maximum gravity separation under test conditions. Study results indicate that satisfactory results are obtained over the range of 0.2 to 0.5 pounds of air per pound hexane soluble materials applied. The anionic emulsificant is the most effective agent in maintaining the oil in solution.

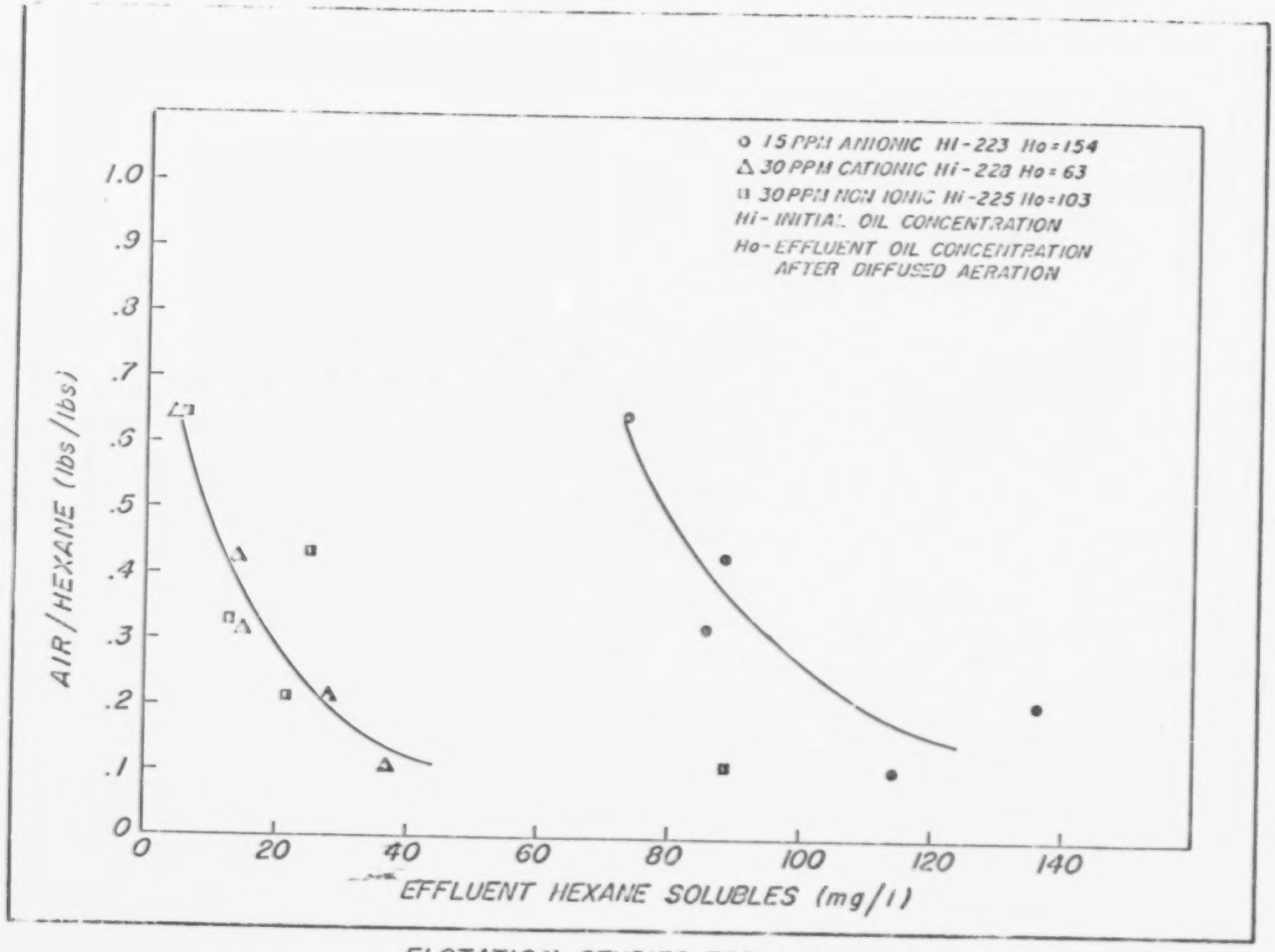
Similar experiments were conducted on refinery waste oils with similar results (see Figure 29). In this case, the anionic emulsifier agent inhibited treatment to a very significant extent and supplemental chemical addition would be required to achieve a process effluent of less than 50 mg/l.

As in the case of chemical treatment, the effluent concentration was generally independent of initial concentration and was principally related to the state of emulsificaton and air to substrate ratio.

Filtration Study

Although the previous techniques demonstrated excellent removal of the oil material, the unit operations would require the possible construction of additional units to the existing treatment facility. However, it may be impractical to consturct such treatment units and other methods would have to be employed to remove the oil materials. One method that could be used would be a continuously or intermittently revolving screening device on which a finely meshed synthetic fiber was constructed. One would place the system at the primary effluent so that clogging due to suspended solids would be minimized. By having the unit operate mechanically, provisions to clean or change the filter could be developed.

A laboratory study was designed to explore the possible use of synthetic fibers as a method for removal of oily materials. The synthetic materials tested included nylon, Dacron, (a tradename of E.I. duPont de Nemours and Company), polypropylene, and acrylic fibers of different mesh sizes. Having eliminated a number of fibers by investigating the materials permeability to water, continuous flow bench scale studies were conducted examining the passage of a synthetic sewage-oil mixture and a primary effluent-oil mixture through the fibers. The test oil was crankcase oil and the synthetic materials tested included an acrylic, nylon, and Dacron* fiber. The plastic tank was divided into two sections by two plastic baffles. Liquid passed from one section to the other through a six-inch hole in the center of the baffles. The baffles were constructed so that the test fiber could easily be placed across this hole and sealed into place using the other baffle. For either mixture, the oil was fed separately into the unit




FLOTATION STUDIES FOR WASTE OIL

FIGURE 29

using the Teflon* tubing arrangement previously described in the biological study section. The hydraulic loading was approximately 15,000 gpd/square foot. Mixing was provided using a diffused air system. Although the oil separation was highly successful the filter medium soon plugged. Attempts were made to reduce the solids buildup by continuously blowing diffused air near the fiber and although this procedure improved conditions, the end effect was the same.

A large amount of oil was eventually adsorbed on the fiber, causing clogging of the test material, and the passage of oil into the effluent. Washing the fiber did not completely remove the oil and passage of the feed solution through the washed fabric was more difficult than in the original system. This condition was observed for both the acrylic and nylon materials. The washing procedure involved cleaning the filter with a mixture of hot water and soap and was the limiting restriction on the use of these materials.

Due to the limited time remaining on the project, further studies were not conducted. These preliminary studies do indicate the possible use of finely meshed fibers to remove oil materials in wastewaters. Extensive laboratory studies involving examining different flow rates, solids levels, fiber mesh sizes, cleaning techniques, fiber surface area, and other characteristics for this type of system would be required to develop such a system. Preliminary experiments were also conducted to determine if this type separation could be employed to capture biological floc escaping secondary clarification during failure conditions. The results were highly successful, capturing essentially all lost floc; however, the clogging problems caused considerable difficulties. It is believed, however, that a successful system can be developed.

## Discussion Of Results

The investigations conducted in the first section of this study indicate that limitation of oily compounds entering an activated sludge system to less than 50 mg/l is desirable. The experiments conducted in this study section indicate that in systems containing a low level of emulsificants, normal sewage, that simple aeration followed by gravity separation will provide the proper separation. A combination of an aeration grit chamber and primary tank with properly designed underflow weirs would provide such a system.

In the case where significant emulsification occurs, dissolved air flotation may be employed for separation of oils. This process, operating in the range of 0.2 to 0.5 pounds of air per pound of hexane soluble material applied will provide an acceptable effluent in all but the most highly emulsified case.

In the extreme case, the addition of any of the chemicals tested in the study result in generation of a satisfactory effluent.

The selection of the final unit operation for any particular case should also be based on cost considerations, including evaluation of the additional cost of sludge handling which results from the new process.

## Study Implications With Respect To Conventional Activated Sludge Treatment

Although the solvent extraction generally employed to describe the oil content of a sewage has limited validity and may include a variety of materials other than heavy oils, this measure will have to be employed until some simple and more accurate method is developed. The study has shown that the resistance of a sludge to upset by loading with an oily compound is a function of the quantity of sludge available to adsorb and assimilate the substrate and the acclimitization of the sludge to the substrate. It is also obvious that the density and settling properties of the sludge before contact with the substrate will have a significant influence on the system performance.

In the case of a shock load the system is unacclimated and the density conditions control the allowable loading. An increase of the sludge hexane level to 5% of the total mixed liquor weight appears to be the maximum safe loading. For a one million gallon flow with usual treatment conditions (2,000 mg/l MLSS and 6 hours detention time) a level of 200 pounds is acceptable while double that level would most certainly cause problems. It appears that whether the load is introduced quickly or over many hours has little effect on the system behavior. If successive slugs occur before the system has returned to normal, either through oxidation of the substrate or by sludge wasting, this effect may be expected to be cumulative.

A system continuously exposed to an oily substrate will be able to tolerate a loading of 0.1 pounds hexane extractable per pound mixed liquor suspended solids. This loading corresponds to a concentration of 50 mg/l in a 2,000 mg/l system, or 75 mg/l at 3,000 mg/l.

In the case of a system that will normally receive higher oil loads settling will fail to be effective but if a more suitable separation system is employed the bacteria may be expected to perform satisfactorily at much higher oil loadings.

The most satisfactory method of protecting a biological system against upset by oily compounds is to exclude these materials,

at concentrations higher than desirable, from the system. The methods of primary oil separation are outlined in the report and present little technical problem. Within the biological system, about the only useful modification is the maintenence of more biological solids under aeration. The solids level must, however, be maintained at a level where the sludge settling properties are good.

In extreme cases, supplemental solids separation, combined with or following secondary settling, can be employed.

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## REFERENCES


1. Beychok, M.R. "Aqueous Wastes from Petroleum and Petrochemical Plants", John Wiley and Sons, London, 1967.

2. "Biological Treatment of Petroleum Refinery Wastes", American Petroleum Institute, New York.

3. Gloyna and Malina, "Petrochemical Wastes Effect On Water", Industrial Water and Wastes, Part I, September-October, 1962, Part II, November-December, 1962, Part III, January-February, 1963, Part IV, March-April 1963.

4. Weston, Merman, and DeMann, "Waste Disposal Problems of the Petroleum Industry", in Industrial Wastes, (ed. Rudolfs) American Chemical Society Monograph 118, Reinhold Publishing Corporation, New York, 1953.

5. Lamkin and Sorg, "American Oil Cleans Up Wastes in Aerated Lagoons", Petroleum Refinery, May, 1964.

6. Roth, Helwig and Hall, "Atlantic Selects Air Flotation for Refinery Waste Treatment", American Petroleum Institute 25th Midyear Meeting, May, 1960.

7. Benger, "The Disposal of Liquid Effluents From Oil Refineries", Fluids Handling, June, 1964.

8. Weston and Merman, "Chemical Flocculation Of A Refinery Waste", American Petroleum Institute 19th Midyear Meeting, May, 1954.

9. Weston, "Separation Of Oil Refinery Wastes" Industrial Engineering Chemical, April, 1950.

10. Ingersoll, "Fundamentals And Performance Of Gravity Separation", Petrol Refinery, June, 1951.

11. McKee, J.E., "Report on Oily Substances and Their Effects on the Beneficial Uses of Water", State Water Pollution Control Board, Sacramento, California, June, 1956.

12. Ettinger, M.B., "Evaluation of Methods Currently Used to Determine BOD, COD and Odor for Industrial Wastes", Sewage And Industrial Wastes, Volume 28, No. 9, Page 1116, September, 1956.

13. Moore, W.A., and Ruchhoft, C.C., "Chemical Oxygen Consumed and Its Relationship to BOD", Sewage And Industrial Wastes, Volume 28, No. 6, Page 705, June, 1951.

14. Elkin, H.F., "Activated Sludge Process Applications to Refinery Effluent Waters", Sewage and Industrial Wastes, Volume 28, No. 12, Page 1112-1116, September, 1956.

15. Elkin, H.F., Mohler, E.F., Jr., and Kumnick, L., "Biological Oxidation of Oil Refinery Wastes in Cooling Tower Systems", Sewage and Industrial Wastes, Volume 28, No. 12, Page 1475, December, 1956.

16. Melpolder, F.W., Warfield, C.W., and Headington, C.E., "Mass Spectrometer Determination of Volatile Contaminants in Water", Analytical Chemistry, Volume 25, Page 1453, 1953.

17. Ettinger, M.B., Moore, W.A., and Lishka, R.J., "Anaerobic Persistence of Phenol and o-Cresol", Industrial and Engineering Chemistry, Volume 43, Page 1132, 1951.

18. Ludzack, F.J., and Kinkead, D., "Persistence of Oily Wastes in Polluted Water Under Aerobic Conditions", Industrial and Engineering Chemistry, Volume 48, Page 263, 1956.

19. Ludzack, F.J., Ingram W.M., and Ettinger, M.B., "Characteristics of a Stream Composed of Refinery and Activated Sludge Effluents" Sewage and Industrial Wastes, Volume 29, No.10, Page 1177, October, 1957.

20. McKinney, R.C., "Microbiology For Sanitary Engineers", McGraw-Hill, New York, 1962.

## GLOSSARY

BOD - Biochemical Oxygen Demand. Standard five day test performed with acclimated seed.

OD - Ultimate Oxygen Demand. Estimated from long term dilution data. Includes both carbonaceous and nitrogenous reactants unless specifically noted separately.

Mixed Liquor Suspended Solids - The total suspended solids concentration in the aeration tank. Includes both inert and active fractions but is assumed proportional to the microbial population.

floc - The individual colonies or groupings within the mixed liquor. Includes microbes, habitat, and detritus.

Hexane Extractable Materials - Those materials which are extractable from a substrate by hexane extractions under defined experimental conditions. The test results will include a wide variety of materials but is usually throught of as describing the concentration of oily materials.

Oily Materials - Insoluble or minimally soluble petroleum components, vegetable oils, animal fats and the like. These materials are usually defined by the hexane extractables test but the efficiency of recovery will vary significantly depending on the nature of the materials.

# APPENDIX

1. Theory of Biological Treatment
2. Chromatography
3. Rapid Chemical Oxygen Demand Test
4. Dissolved Oxygen Uptake Rate
5. Sedimentation
6. Flotation Procedure
7. Standard Jar Test Procedure

# THEORY OF BIOLOGICAL TREATMENT

Biological treatment is used to reduce the organic concentration in a waste. It is a process wherein active bacteria mixed with a waste under suitable environmental conditions reduce the waste to a more stable form. When the reaction proceeds in the presence of sufficient dissolved oxygen, the system is aerobic and the final decomposition products are carbon dioxide and water. Two basic phenomena occur when organic matter is removed by microorganisms. Oxygen is consumed by the organisms for erespiration and new cell mass is synthesized. The organisms also undergo progressive auto-oxidation of their cellular mass.

Wastes can contain suspended, colloidal, and dissolved organics. The organic matter is measured by the Biochemical Oxygen Demand (BOD) or by the Chemical Oxygen Demand (COD). The BOD may be defined as the amount of oxygen required by suitable organisms in the stabilization of a given quantity of organic matter. Theoretically, an infinite time is required for complete biological oxidation of organic matter, but for practical purposes, the reaction may be considered complete in twenty days. The conventional BOD test is a measure of the quantity of oxygen utilized in the first five days of oxidation, under standard conditions, and is designated as $BOD_5$. The quantity of oxygen required to satisfy the twenty day demand is usually referred to as ultimate $BOD_u$. In the COD determination, organic matter is converted to carbon dioxide and water regardless of the biological assimilability of the substances. In the analysis of data, it must be remembered that some materials which are chemically oxidized will not be biologically oxidized.

Biological waste treatment, then, essentially consists of controlling environmental factors to enable a mixed microbial culture to use the organic matter as a food source for reproduction (synthesis) and energy (assimilation). In aerobic treatment systems, organisms are suspended in a liquid medium with the waste to be treated. Dissolved oxygen is required by the culture and sufficient time is allowed for the organisms to utilize the organics as a food source. Figure A-1 graphically represents the occurring biochemical phenomena. The suspended and colloidal organic matter measured as BOD undergoes an initial reduction by adsorption to the organisms.

In general, the system will approach some minimum BOD value rather than zero concentration, due to an equilibrium established between the bacteria and their liquor. The magnitude of the initial removal is a function primarily of the microbial concentration, acclimatization, and waste composition. The rate of reaction is a function of temperature, nutrient level, concentration of both the waste and microbial population.

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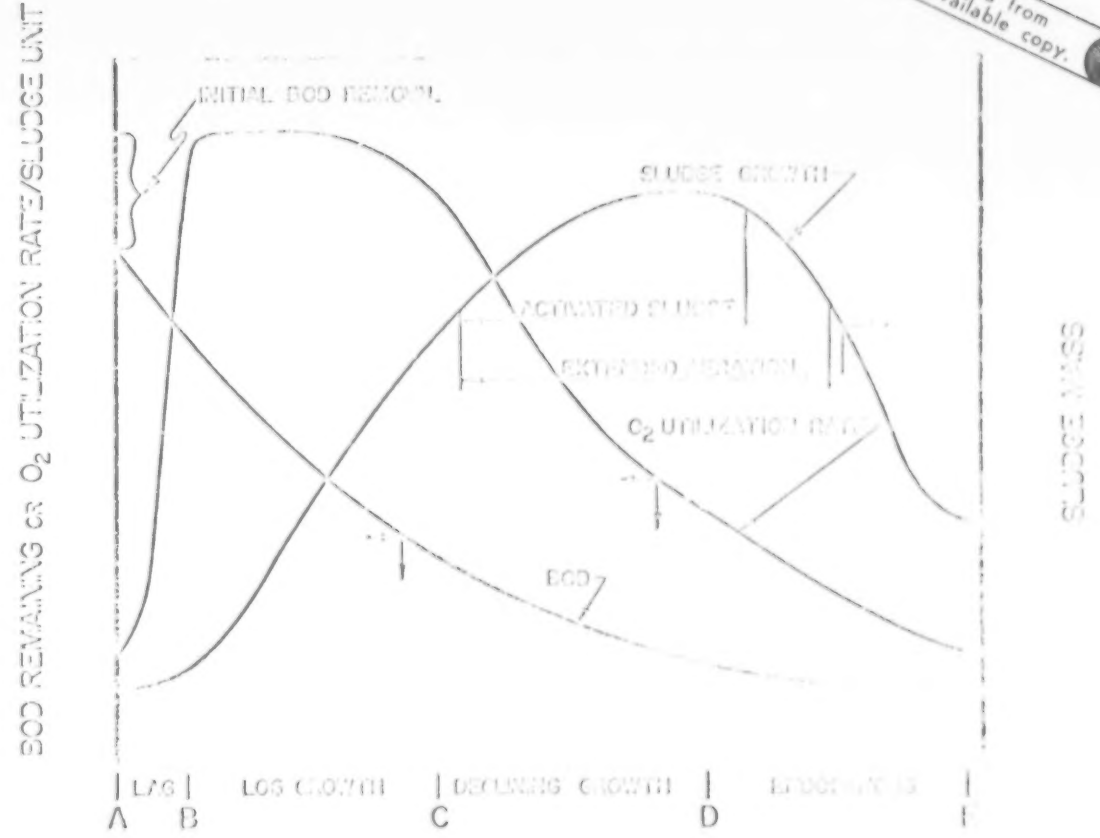



FIGURE A-1

SCHEMATIC REPRESENTATION OF BIOLOGICAL TREATMENT PROCESS

Microbial growth may be considered in the following steps (see Figure A-1): first, a lag period in which the culture adapts from its previous environment to the present; second, a period of maximum growth under conditions where unlimited food is available; third, a period of declining growth where food availability finally becomes a limiting condition and the organisms consume previously stored food; and finally, an endogenous phase where under severely limited food conditions, cells die and are, in turn, consumed so that mass population is reduced. The final mass of organisms is always more than the initial because certain non-biodegradable materials are generated during synthesis. The oxygen utilization rate per unit weight of microorganisms is low at first, quickly reaching a maximum. As the competition for food becomes more acute, the rate decreases until an endogenous level of demand is reached. A knowledge of the parameters governing these reactions is necessary in the design of a biological system to treat any organic waste.

The biochemical phenomena can be illustrated by the following general relationships:

Synthesis:

$$[\text{organic matter}]+[\text{oxygen}]+[\text{nutrients } NH_3,\ PO_4,\ \text{etc.}] \xrightarrow{\text{cells } r_1} [\text{new cells}]+[CO_2]+[H_2O] \quad (1)$$

Respiration:

$$[\text{cells}]+[\text{oxygen}] \xrightarrow{r_2} CO_2 + H_2O + NH_3 \quad (2)$$

where:

$r_1, r_2$ = denotes rate of reaction associated with Equations (1) and (2)

In the design of waste treatment facilities, the rate at which these reactions occur, the amount of oxygen and nutrient required, and the quantity of organisms produced in the system must be determined.

The rate of reaction for Equation (1), $r_1$, is a function of the reactants (organic matter, oxygen, nutrients) and in some cases, the amount of cells present in the system. A reaction rate which is a function of the reactants and products is described as an autocatalytic reaction. In most biological systems, the nutrients and dissolved oxygen are present in excess so that the rate of reaction is only a function of the organic matter and/or microorganisms present in the environment. Many

biological systems, such as activated sludge, operate under a high microbial load such that the reaction rate is only a function of organic material present and is defined as a first order rate with respect to organic material. Therefore, the rate of reaction for Equation (1) can be expressed:

$$r_1 = K_1 L \tag{3}$$

where:

$L$ = organic material present in the system (usually expressed as mg/l $BOD_5$).

$K_1$ = reaction rate constant and is a function of temperature only.

Applying similar analysis for Equation (2), the rate of reaction can be expressed as:

$$r_2 = K_2 M \tag{4}$$

where:

$M$ = amount of organisms present in the system (usually expressed as mg/l suspended solids)

$K_2$ = reaction rate coefficient and is a function of temperature only.

Therefore, the rate of formation for the organic matter, oxygen, and cells can be expressed as:

Organic Matter:

$$\frac{dL}{dt} = -K_1 L \tag{5}$$

Oxygen:

$$\frac{dO_2}{dt} = -a'K_1 L - b'K_2 M \tag{6}$$

Cells:

$$\frac{dM}{dt} = aK_1L - K_2M \qquad (7)$$

where:

a' = conversion factor (stoichiometric coefficient) relating organic matter to oxygen;

b' = conversion factor (stoichiometric coefficient) relating cells to oxygen;

a = conversion factor (stoichiometric coefficient) relating organic matter to cells.

minus sign (-) indicates removal

Equation (5) describes the removal of organic material by microorganisms. Clearly in many systems, microorganisms produce organic by-products that are used by other organisms as food sources. In this development, the general term, organic matter, includes not only the initial food sources but also organic by-products. However, as previously mentioned, the experimental techniques used to measure this term (BOD and COD tests) determine the overall organic material in the system and not the individual compounds.

Equation (6) relates the amount of oxygen consumed to the oxygen required for synthesis and the oxygen required for the endogenous respiration of the microbial population. The accumulation of cells in a biological system [Equation (7)], is due to synthesis of new cells as the organic material is removed and the subsequent respiration of these cells due to the lack of an exogenous food source in the system. The three equations [Equations (5),(6), and (7)], describe only the biochemical phenomena occurring in a biological system where the rate of reaction of Equation (1) is a function of only the organic matter present and the rate of reaction for Equation (2) is a function of only the organisms present in the system. For batch systems, these relationships describe the overall activity in the unit. However, in continuous flow units, mass balances must be carried out on the entire system and the kinetic expressions are just one term of the total mass balance.

In analysis of biological systems, investigators are principally interested in relating the amount of organics removed to

the amount of oxygen utilized and to the amount of cells produced. Expressions for these parameters are developed using Equations (5), (6) and (7), and the following relationships:

$$L = L_i - L_r \tag{8}$$

$$O_2 = O_{2i} = O_{2r} \tag{9}$$

which relate the organic matter and oxygen remaining ($L$, $O_2$) to the initial concentration ($L_i$, $O_{2i}$) and the amount removed ($L_r$, $O_{2r}$). The rate of change of these relationships is:

$$\frac{dL}{dt} = \frac{dL_i}{dt} - \frac{dL_r}{dt} \tag{10}$$

and

$$\frac{dO_2}{dt} = \frac{dO_{2i}}{dt} - \frac{dO_{2r}}{dt} \tag{11}$$

Since the initial concentrations do not change with time, the rate functions can be expressed as:

$$\frac{dL}{dt} = - \frac{dL_r}{dt} \tag{12}$$

and

$$\frac{dO_2}{dt} = - \frac{dO_{2r}}{dt} \tag{13}$$

Therefore, Equations (5), (6), and (7) can be modified to relate these expressions to removal as follows:

$$\frac{dL_r}{dt} = K_1 L \tag{14}$$

$$\frac{dO_{2r}}{dt} = a' K_1 \frac{dL_r}{dt} + bK_2 M \tag{15}$$

$$\frac{dM}{dt} = aK \frac{dL_r}{dt} - K_2 M \tag{16}$$

These relationships are specific for the initial assumptions imposed on the system for the definitions of the rates of reaction, namely Equations (3) and (4).

Along with Equations (15) and (16), another relationship is used to describe the removal of organic material in a completely mixed continuous flow reactor and includes a term for the biochemical kinetics. This relationship for the steady-state condition is:

$$QL_i - QL - VK_1L = 0 \tag{17}$$

or:

$$\frac{L}{L_i} = \frac{1}{1 + \tau K_1} \tag{18}$$

where:

$Q$ = volumetric flow rate ($L^3/t$)

$L_i$ = inlet organic concentration ($BOD_5$) ($Mass/L^3$)

$L$ = outlet organic concentration ($BOD_5$) ($Mass/L^3$)

$V$ = volume of reactor ($L^3$)

$K_1$ = reaction rate coefficient (1/day)

$\tau$ = V/Q hydraulic detention time (t)

Also, the oxygen required and cells produced due to the removal of the organics can be expressed:

$$\#O_2 \text{ required/day} = a'\#BOD_5 \text{ removed/day} + b'\#S_a \tag{19}$$

where:

$a'$ = fraction of the $BOD_5$ removed which is used to provide energy for growth;

$b'$ = endogenous respiration rate coefficient

$S_a$ = cells under aeration

$$\#\text{ cells accumulated/day} = a\#BOD_5 \text{ removed/day} - bS_a \tag{20}$$

where:

| | | |
|---|---|---|
| a | = | fraction of $BOD_5$ removed which is synthesized to new biological cells; |
| b | = | fraction of cells under aeration which are oxidized; |
| $S_a$ | = | cells under aeration. |

This development demonstrates the continuity between batch and continuous systems. Although the time dependent terms are different, the biochemical kinetic expressions are equivalent and, therefore, batch studies serve a distinct purpose of conveniently providing a simple system to estimate the biochemical kinetics and stoichiometric coefficients. However, the use of a batch system requires strict experimental techniques but is (or could be) an excellent technique for determining the biochemical kinetics. At present, continuous information is used to estimate the biological coefficients by employing the relationships given by Equations (18), (19), and (20).

The present discussion has been based on the premise that the organic material was in a state which the organisms could easily metabolize. However, in some instances, complex organic compounds such as suspended or colloidal materials enter a biological system and are subject to degradation. For organisms to metabolize these materials, enzymes have to be generated that are capable of attacking these complex compounds and reducing them to a form which can be passed into the cell. Hydrolysis of complex materials can be time-consuming and can easily be the controlling mechanism in the biochemical phenomena occurring. Therefore, in addition to Equations (1) and (2), another relationship must be used to describe the enzymatic process required to breakdown complex compounds. This reaction can be expressed by the following general relationships:

$$\left[\begin{matrix}\text{complex}\\ \text{organic}\end{matrix}\right]+\left[\begin{matrix}\text{nutrients}\\ \text{oxygen}\end{matrix}\right]+[\text{enzyme}] \xrightarrow{r_3} \left[\begin{matrix}\text{organic}\\ \text{enzyme}\\ \text{complex}\end{matrix}\right]+\text{products} \qquad (19)$$

$$\left[\begin{matrix}\text{organic}\\ \text{enzymatic}\\ \text{complex}\end{matrix}\right]+\left[\begin{matrix}\text{nutrients}\\ +\ \text{oxygen}\end{matrix}\right] \xrightarrow{r_4} [\text{enzyme}] + \left[\begin{matrix}\text{soluble}\\ \text{organic}\end{matrix}\right] + [\text{products}] \qquad (20)$$

If the rate of generation of the complex material is very low compared to the removal of organic matter (i.e., $r_3 > r_1$ and/or $r_4 > r_1$), the organic removal will be controlled by the microorganisms ability to generate enzymes to hydrolyze the

complex materials. In some cases involving high weight carbon compounds, organisms can only generate enzymes that partially degrade these materials resulting in the formation of an organic product that is commonly labeled "non-biodegradable". Acclimation of a microbial population to a waste results in the formation of the required enzymes. However, even after a careful acclimation procedure, some organic compounds are too complex, so that only partial reduction occurs.

This study explored both phenomena; that is, the removal in the same biological system of both soluble simple organic materials and high weight organic compounds. The simple organic material was a mixture of easily degradable organic compounds (synthetic sewage) fed in parallel with high weight insoluble materials. In addition, a control unit fed only the synthetic unit was monitored for organic removal and oxygen utilization. By comparing the organic removals and oxygen utilization, conclusions could be drawn regarding the assimilatory capacity of the biological population.

# GAS CHROMATOGRAPHIC STUDY

## Introduction

In an attempt to develop a more acceptable method of identifying the test compounds, a study was undertaken to monitor them using gas chromatography. Although the extraction technique is commonly used in wastewater analysis and yields valuable information concerning the removal of total oil material, this method is too general when information is required concerning the removal of individual compounds associated with an oil material. In addition, the extraction method requires a large sample volume (at least 100 ml) and this presents a difficulty in many studies. A gas chromatograph employing small sample sizes (1 µl) could be used in all applicable studies. Information gained from a truer knowledge of the compounds consumed by the microbial population would aid greatly in determining carbon balances on the system, the oxygen requirements per mass of carbon removal, and estimating at what point (i.e., at what carbon level) microorganisms are inhibited from synthesizing new cells.

## Studies

An investigation was conducted to determine the most convenient methods to measure the individual compounds associated with the test materials. A detailed literature search and discussions with chromatographic research group of several petroleum companies yielded two possible gas chromatographic methods. They are:

### 1. Precolumn Technique

The precolumn would be heated to 200°C and a sample would be injected. All the compounds present in the oil sample that vaporize at temperatures less than or equal to 200°C would evaporate from the precolumn into a dual column an would be separated and detected. The physical design of the precolumn and the surrounding valving and piping would be extremely delicate and would required a great deal of work. However, a simplified but informative procedure was suggested relating carbon number to boiling points.

### 2. Boiling Point Technique

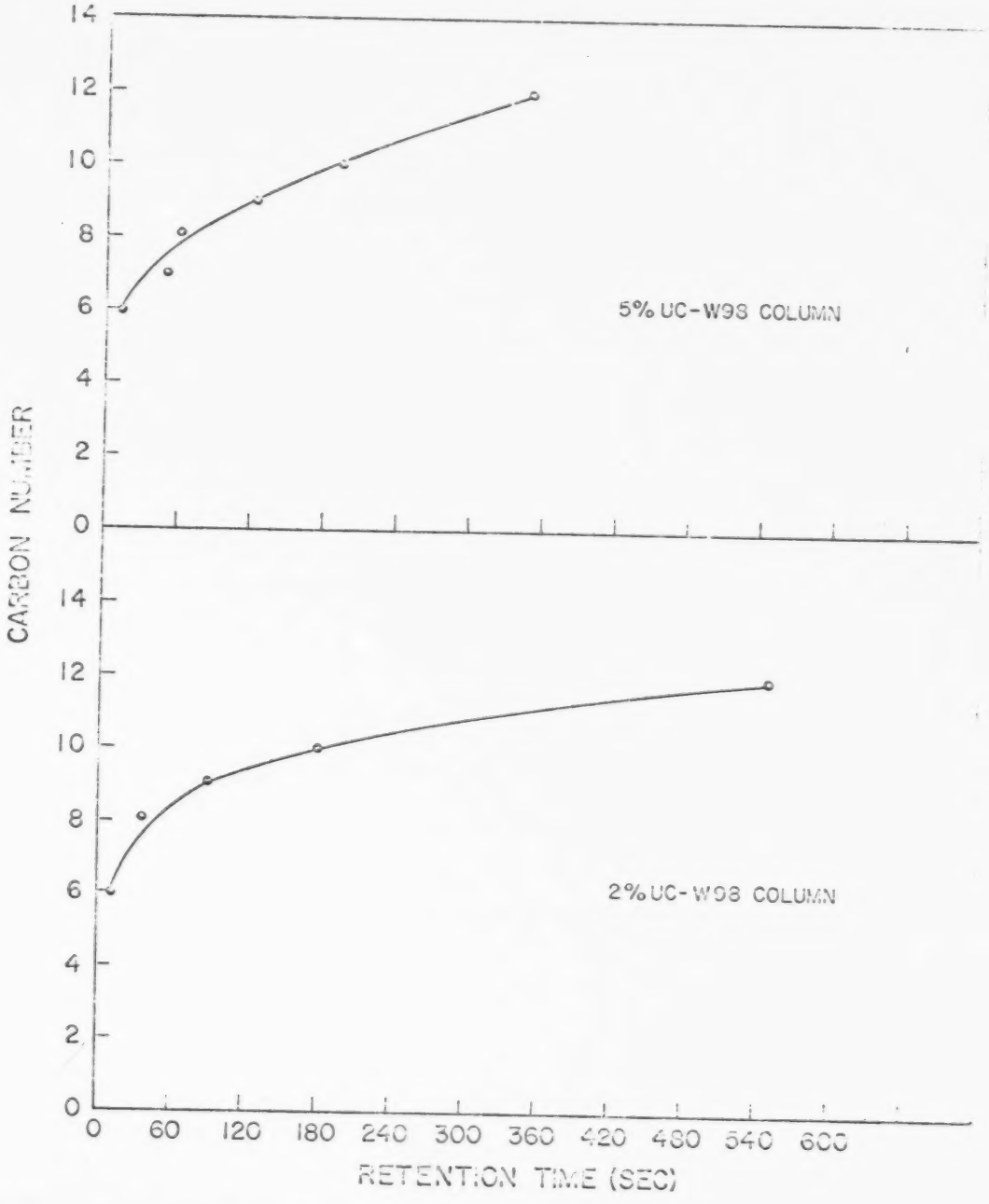
This procedure could be simply characterized as a gas chromatographic distillation of oil

compounds. A sample introduced into the gas chromatograph is separated into individual compounds according to the boiling point. The column temperature is raised at a known rate and the areas under the chromatogram and chromatogram peak heights are recorded. A calibration curve covering the boiling points expected from a test sample is constructed from a standard mixture of low weight hydrocarbons. The curve consists of carbon number plotted on the ordinate axis and the associated retention time on the abcissa axis. Comparison of the initial and final chromatogram of the test sample would yield the fraction of oil material that has been metabolized.

In view of the diverse nature of the oil samples, a detailed analysis of the individual compounds would have been extremely time-consuming and would digress from the purpose of the study. However, knowledge of the fractional amount of particular low weight carbon materials that can be degraded would be very helpful and, therefore, the boiling point technique was selected.

Studies were carried out testing this technique and establishing an accurate and precise sampling method. The instrument was a Perkin-Elmer Model 881 with flame ionization detector and linear temperature programming. The columns used in this study were a 2% UC-W98 Chrom W-DMCS and a 5% UC-W98 Chrom W-DMCS (2 feet long). The first investigation was to obtain calibration curves for the two columns. The standard mixture consisted of hexane, heptane, octane, nonene, decane, dodecane, and ercosane. Typical outputs are shown on Figure A-2 for the 2% and 5% columns and demonstrate the better results obtained on the 5% column.

Studies were then carried out on samples of crude and crank case oils testing their resolution with and without the use of a solvent. Typical results are shown on Figure A-3 (a thru d) for these two compounds. The Figure shows that crude and crankcase oil samples had good resolution of the major peaks up to 250°C and many components were vaporized before 200°C. The crude oil sample had a homologous series with isomers, while the crankcase oil sample did not have any regularity and probably consisted of more randomly cracked hydrocarbons and oxidation products. Comparing the two chromatograms, the crankcase oil sample seemed to have fewer and smaller amounts of hydrocarbons based on peak heights and the number of peaks. No attempt was made to identify the individual components in




CARBON NUMBER VS RETENTION TIME (SEC)

FIGURE A-2

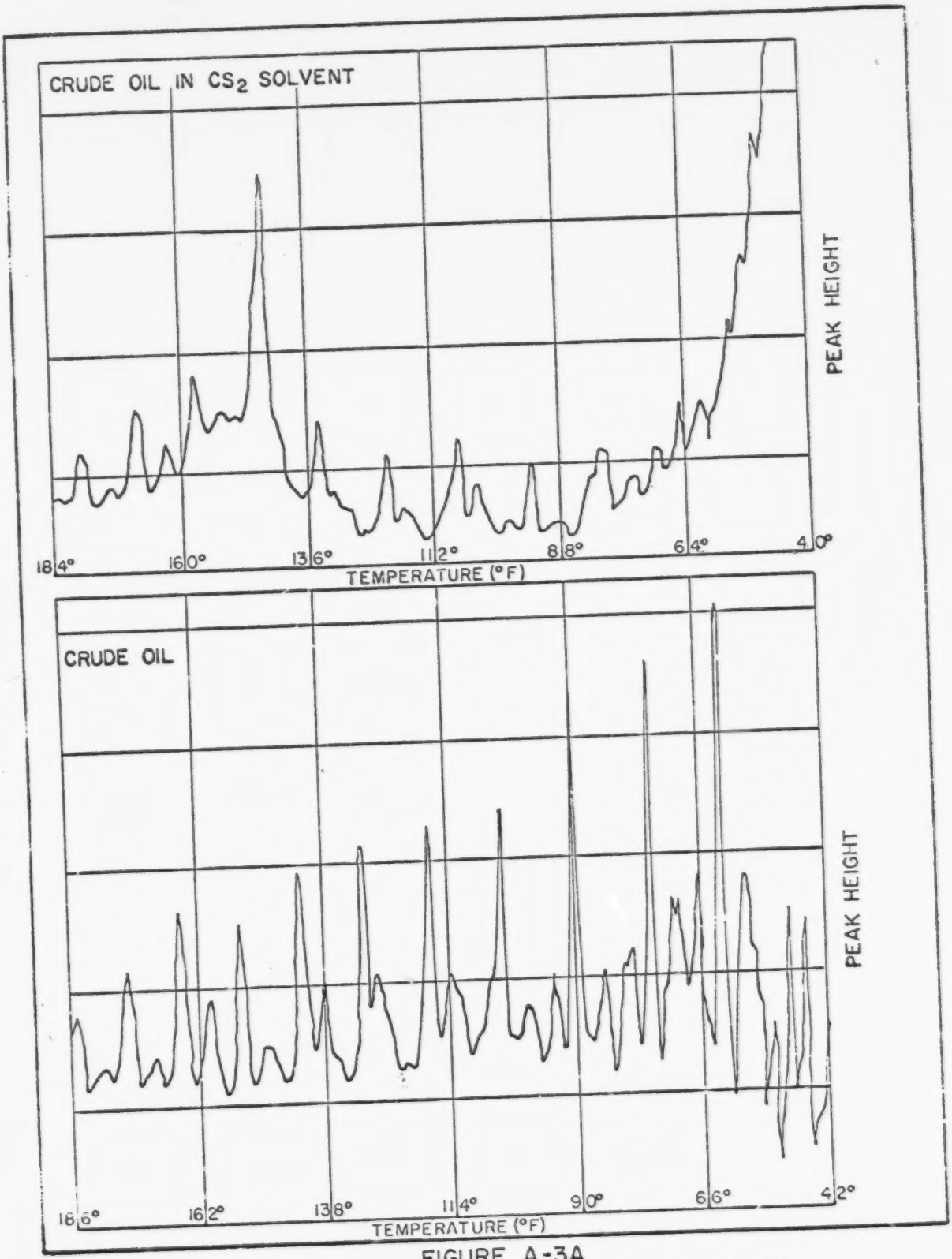



FIGURE A-3A
GAS CHROMATOGRAPHY RESULTS FOR CRUDE OIL

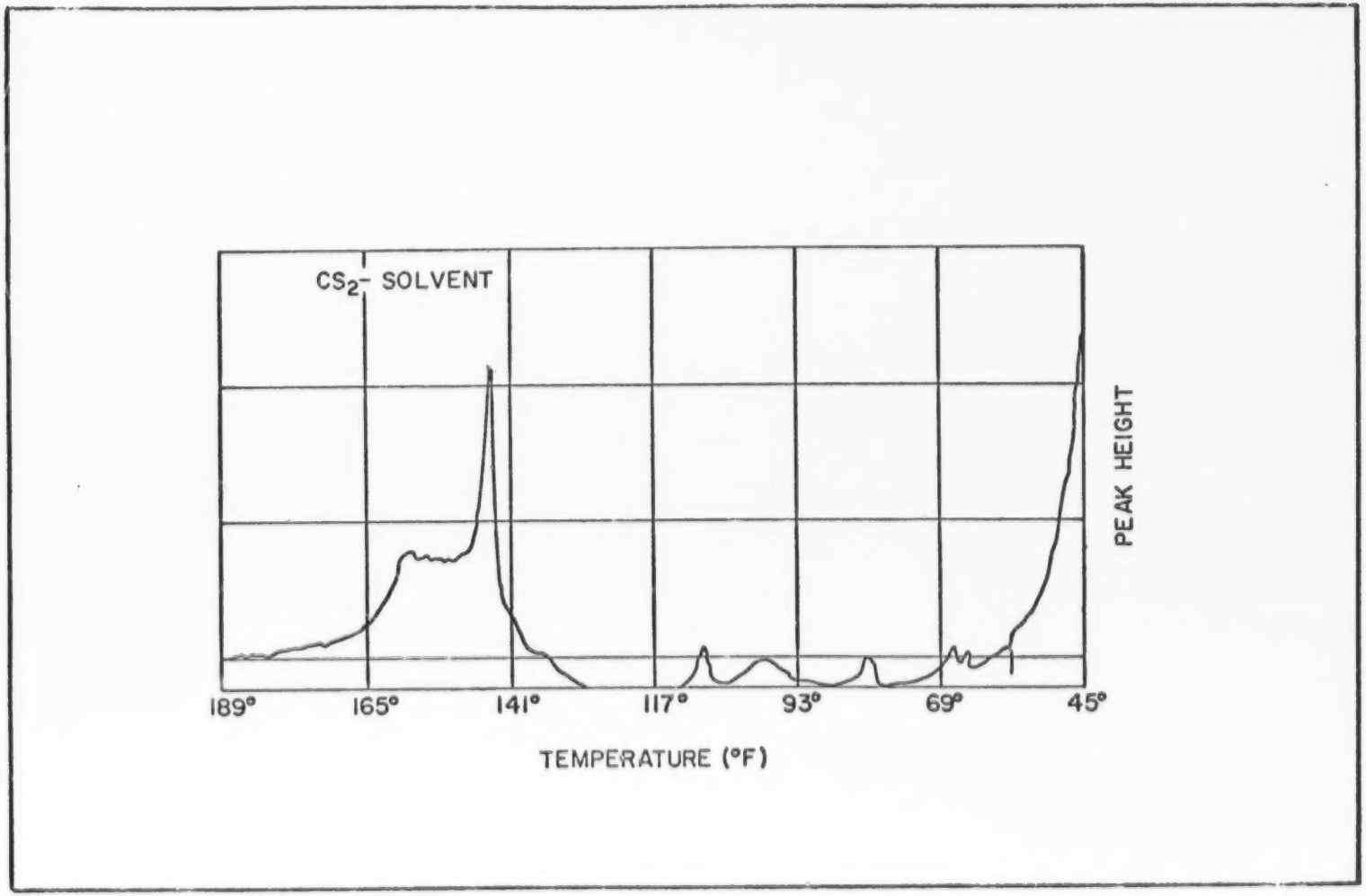



FIGURE A-3B

GAS CHROMATOGRAPHY OUTPUT FOR CARBON DISULFIDE

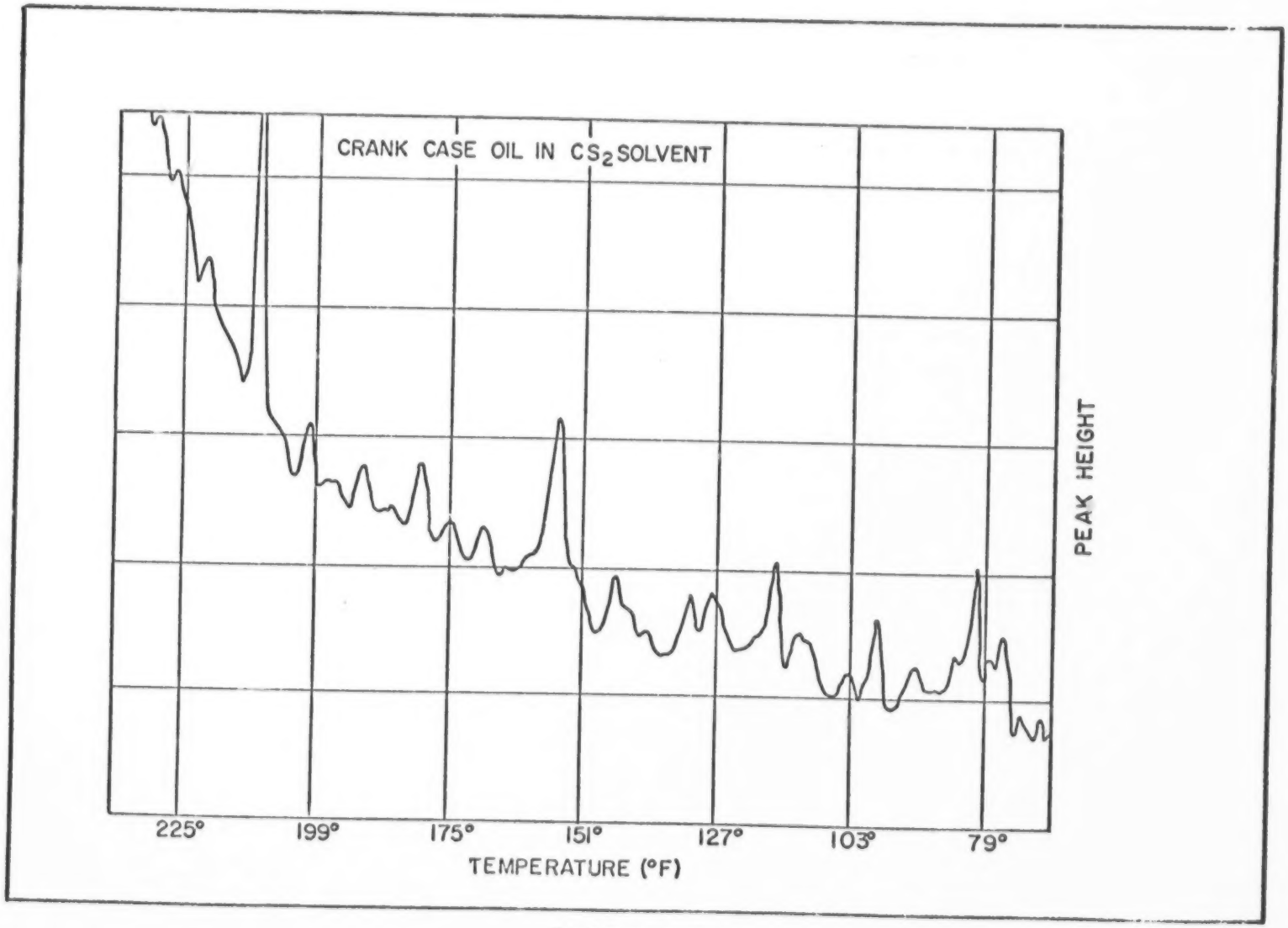



FIGURE A-3C

GAS CHROMATOGRAPHY RESULTS FOR CRANKCASE OIL IN $CS_2$ SOLVENT

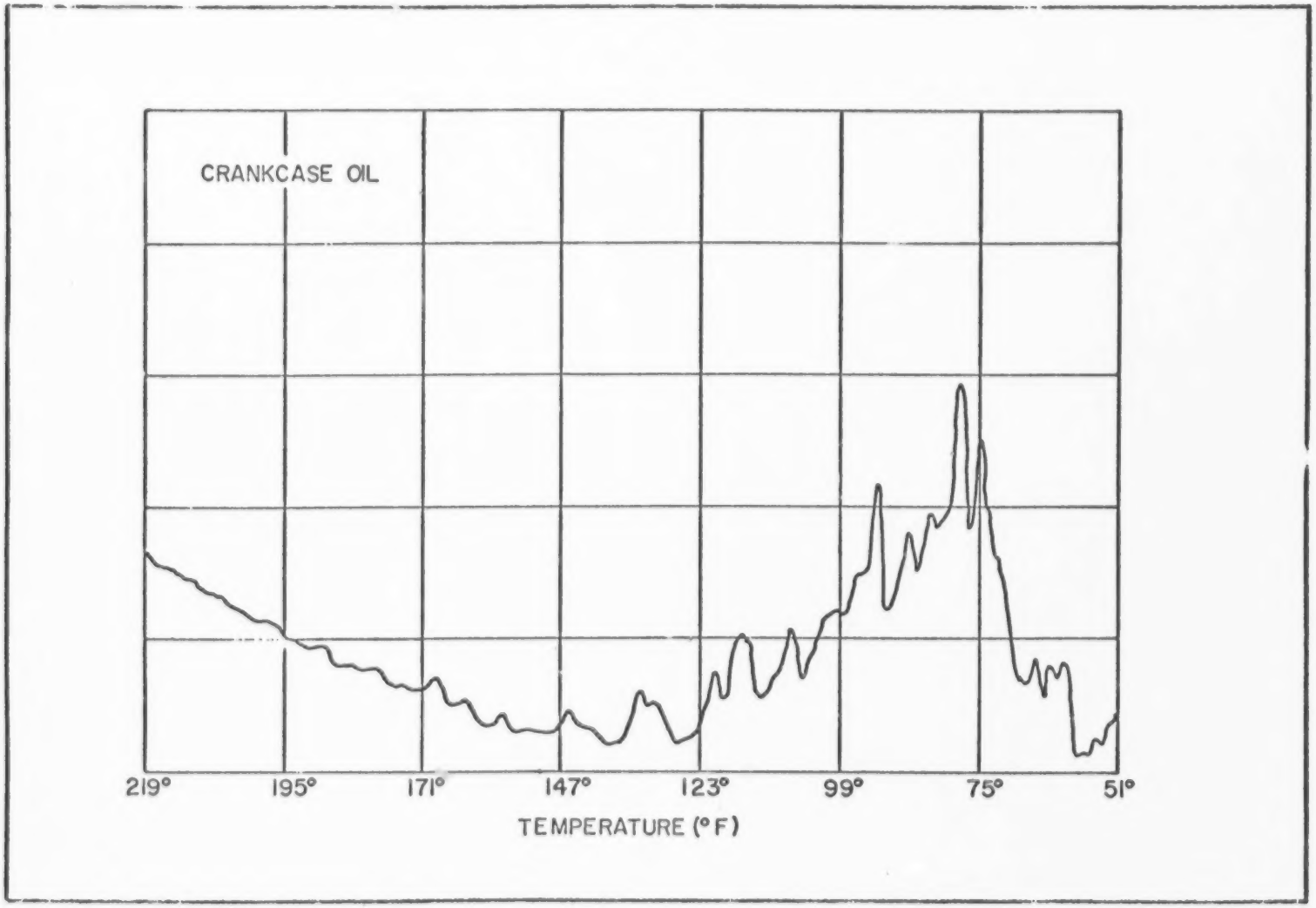



FIGURE A-3D

GAS CHROMATOGRAPHY RESULTS FOR CRANKCASE OIL

either crude or crankcase oil, since a chromatographic "fingerprint" could serve as an indicator of the oil breakdown in biological system.

Having tested the crude and crankcase samples, a study was set up to develop an accurate and reproducible sampling technique. The tests included selection of the more reliable solvent, the type of sampler to use, the reproducibility of injection, the reproducibility of extraction, the stability of extraction, the effect of large concentration of test materials on the chromatographic output, and finally, the effect of large sample volumes on the output.

The first and most crucial step in this study was to develop an accurate and reproducibly technique to sample the oil-water interface. Experiments were conducted to select the solvent that extracted the largest fraction of the test compound. Crankcase oil was selected as the test compound. The study is summarized as follows:

1. A 5 µl of oil was pipetted into 50 ml water and mixed. The concentration of the mixture was approximately 100 mg/l.

2. A 1.0 ml of the test solvent was added to the oil-water mixture. The test solvents were carbon disulfide, diphenylbenzylamine, and hexane.

3. A 1.0 µl sample was extracted from the mixture and injected into the gas chromatograph.

4. The conclusions from this study were:

   a) Althouqh diphenylbenzylamine has a high boiling point (300°C) and peaks after the compounds of interest, it is unsatisfactory because of low boiling compounds monitored in the solvent. The solvent seemed to contain impurities that would have to be reved.
   b) Hexane has a boiling point of 69°C but did not extract a large portion of the components from the crankcase oil when compared to the number of peaks observed from the carbon disulfide extraction. In addition, two detectable impurities

were present in large quantities in this solvent.

c) Carbon disulfide was the best solvent of those tested because it extracted more material; had fewer and smaller amounts of impurities (a peak at 140°C); had a low boiling point (46°C) so that other low boiling point components would not be dampened out by the solvent peak.

Tests were also run to determine the reproducibility of different injections of the same extraction and the reproducibility of different extractions. In addition, studies were conducted on the volume of solvent, the different sample sizes, and other pertinent variables in order to establish a reliable sampling program. The results from the experiments were:

1. Injections of the same extraction were reproducible in general, although sometimes spurious peaks did appear. It is advisable to inject all samples at least twice. Extracts must be tightly stoppered to prevent evaporation of solvent and components.

2. Extractions were reproducible but were very dependent upon the technique used to remove the oil from the water. Also, the initial temperature must be controlled, otherwise the programmed temperature will be inaccurate and the apparent retention times of the components will change. In general, greater recovery of the oil could be achieved if the oil slick were in a small area.

3. An extraction with 4 ml disulfide rather than 2 ml showed no significant difference in recovery.

4. Extracts were stable overnight if stored in tightly stoppered test tubes.

5. Doubling the oil concentration (i.e., 20 ml instead of 10 ml) resulted in peak heights two to three times greater and therefore had more definable resolution of the smaller peaks which were barely discernable with a 10 ml of oil.

Having defined the basic sampling technique, a study was set up to test this procedure in a biological system and to observe the possible biochemical breakdown of the crankcase oil. Batch biological units were set up in one liter reaction vessels aerated with diffused air. The reactors contained an acclimated seed, dilution water containing the basic nutrients, and 200 mg/l crankcase oil. The turbulent mixing conditions caused the oil to adhere to the walls and accurate recovery was impossible. Attempts were made to coat the glass walls with a hydrophobic substance in which the oil would wet the walls and drop back into the liquid. Materials tested were paraffin wax, silicone, stopcock grease, scotchguard* fabric stain repellent, and Teflon** dry lubricant. The results demonstrated that these materials exhibit wetting properties similar to glass. Other studies included setting up biological units in polyethlyene containers but, as before, the oil adhered to the wall.

To improve the reproducibility of experiments a measurement system employing the Gilson respirometer was set up to monitor the degradation of crankcase oil. Complete mixing in the liquid phase was provided by mechanically shaking the flasks at a low shake rate (60 cpm) and with this technique it was assumed that oil adsorption on the cylinder wall would be minimized. For this study, the oil was initially weighed out on glass cover slips and was placed in the respirometer flasks. Although some adherance to the walls was observed, it was possible by extracting the entire flask contents, to obtain reasonable samples.

When results were obtained, it was found that little interpretation was possible. The change in the total area was small, relative to the mass present, and more importantly, "cracking" appeared to be going on with the chromatograph.

Exploration of this phenomena with experts in petrochemical analysis concluded that what was observed was quite possible and in fact, probable. A variety of possible solutions to the problem were explored, but in view of the project limitations, no additional studies were conducted.

# CONCLUSIONS

1. The qualitative identification and quantitative measurement of low carbon number compounds may be easily accomplished using gas chromatography.

2. The isolation of higher carbon compounds requires special study techniques to overcome "cracking" within the chromatograph.

3. The project was not able to extract and separate oily compounds from biological floc.

4. Chromatography shows significant promise as a superior technique for such studies, but considerable further work would be required to develop suitable methods and procedures.

## 3. Rapid Chemical Oxygen Demand Test

REAGENTS

1. Standard Potassium Dichromate solution 0.05 N. Take 2.4518 grams $K_2Cr_2O_7$ primary standard grade that has been previously dried at 103°C for two hours and dissolved in distilled water. Make up solution to 1,000 ml with distilled water.

2. Standard Ferrous Ammonium Sulfate solution 0.05 N. Dissolved 19.6 grams $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml concentrated $H_2SO_4$, cool and dilute to 1,000 ml. This solution must be standardized against the $K_2Cr_2O_7$ DAILY.

   Standardization; Dilute 25.0 ml standard dichromate solution to about 250 ml. Add 20 ml concentrated $N_2SO_4$ and allow to cool. Titrate against the ferrous ammonium sulfate using 5 to 6 drops of ferrion indicator.

$$N = \frac{\text{ml } K_2Cr_2O_7 \times 0.05}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

3. Sulfuric Acid concentrated.

4. Ferrion indicator solution: dissolve 1.485 grams 1.19 phenanthroline monohydrate, together with 0.695 grams $FeSO_4.7H_2O$ in water and dilute to 100 ml. This indicator solution may be purchased already prepared.

5. Oxidizing solution: dissolved 2.4518 grams of $K_2Cr_2O_7$ in a mixture of 500 ml phosphoric acid $H_3PO_4$ concentrated and 500 ml sulfuric acid concentrated $H_2SO_4$.

6. Silver sulfate.

7. Mercuric sulfate.

PROCEDURE

A quantity of waste matter or an aliquot of a dilution thereof according to the concentration of the waste is added to 25 ml of oxidizing solution in a 500 ml flask. A speck of

silver sulfate (catalyst) is added, followed by 1/3 teaspoon of mercuric sulfate (in the presence of halogens). This mixture is heated to 168°C. (Caution: this material must not be allowed to heat over (170°C). Cool and dilute to approximately 250 ml. Titrate against ferrous ammonium sulfate using 5 to 6 drops of ferrion indicator.

A blank consisting of a volume of distilled water equal to the sample together with the reagents is run in a similar manner.

CALCULATION

$$\text{mg/l COD} = \frac{(a-b)c \times 8{,}000}{\text{ml sample}}$$

COD = Chemical Oxygen Demand

a = ml $Fe(NH_4)_2(SO_4)_2$ used for blank

b = ml $Fe(NH_4)_2(SO_4)_2$ used for sample

c = normality $Fe(NH_4)_2(SO_4)_2$

Estimate of Sample Volume

Using esimate value of COD and a desired delta titration (a-b) of 10, then the estimated sample volume would be:

$$\text{Estimated sample volume} = \frac{4{,}000}{\text{estimated COD}}$$

Using this sample volume and the procedure above to determine the actual COD.

4. Dissolved Oxygen Uptake Rate

1. Before initial use, the dissolved oxygen probe should be cleaned, standardized and allowed to stand in distilled water overnight. The probe membrane should be replaced if punctured or if frequent calibrations or drifting of the meter is noted. Usually, the membranes must be replaced at two to three week intervals.

2. Fill BOD bottle to overflowing with sample so that there are no air bubbles entrapped in the liquid.

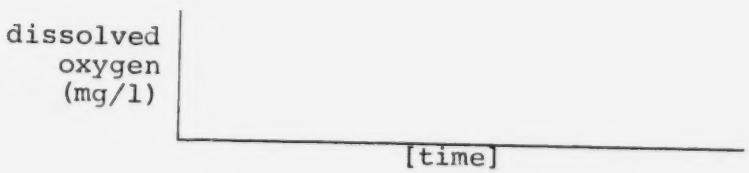
3. Insert magnetic mixing bar, and place bottle on magnetic mixer. Measure initial temperature of sample.

4. Insert dissolved oxygen probe so that no bubbles remain in the bottle an airtight seal is formed. Be sure sufficient velocity (not less than 1 fps) is maintained past the probe head.

5. Record the drop in dissolved oxygen reading with time, time zero being the start of meter drop-off. Measure the final temperature of the sample and use average temperature for determining the saturation value of dissolved oxygen for probe calibration.

6. Initial dissolved oxygen reading should be 80 to 90 percent of oxygen saturation for that temperature. Samples may have to be vigorously shaken in the BOD bottle, about three-quarters full, to achieve the desired dissolved oxygen before the measurement begins.

7. Plot the dissolved oxygen concentration (not meter reading) versus time on rectangular coordinate paper.




8. The oxygen uptake rate is the slope of the straight line formed on the previous plot. The units should be converted to mg/l/hour.

$$\text{Oxygen uptake rate} = \frac{\text{change in dissolved oxygen}}{\text{change in time}} = \text{mg/l/hour}$$

## 5. Sedimentation

Solids-liquor separation is an integral part of biological treatment systems. The primary function of sedimentation is to separate biological growths from their associated treated liquor for return to the aeration process for subsequent disposal.

In settling, the sludge floc agglomerates and the mass particles settles as a blanket forming a distinct interface between the floc and the supernatant. Often, due to solids concentration and the waste characteristics, a "lag" period occurs during which the sludge undergoes an initial period of flocculation. Figure A-4 is a typical settling curve. The sludge settles at a uniform velocity until the settling interface approaches an interface of critical concentration. The magnitude of this velocity is a function of the initial solids concentration. Free settling (A) will not exist beyond this critical solids concentration. At this point, a transition zone (B) occurs, and the settling velocity decreases due to the increasing density and viscosity of the suspension around the particles. A compression zone (C) occurs when the floc concentration becomes so great as to be mechanically supported by the layers of floc below. The solids concentration in the compression zone will be related to the depth of sludge and the detention of the solids in the zone.

The settling rate is determined from a plot of the height of the sludge interface with time. The settling velocity is converted to an Overflow Rate (O.R.).

$$O.R.(gal/day/sf) = V_s(ft/hr) \times 180$$

The hydraulics of inlet and outlet devices are of significant importance in the settling process. The usual limitation, imposed by the hydraulic consideration, is the overflow rate. Scale up factors are required to convert laboratory scale settling data to plant scale. A factor is normally used to reduce the laboratory overflow rate to plant scale.

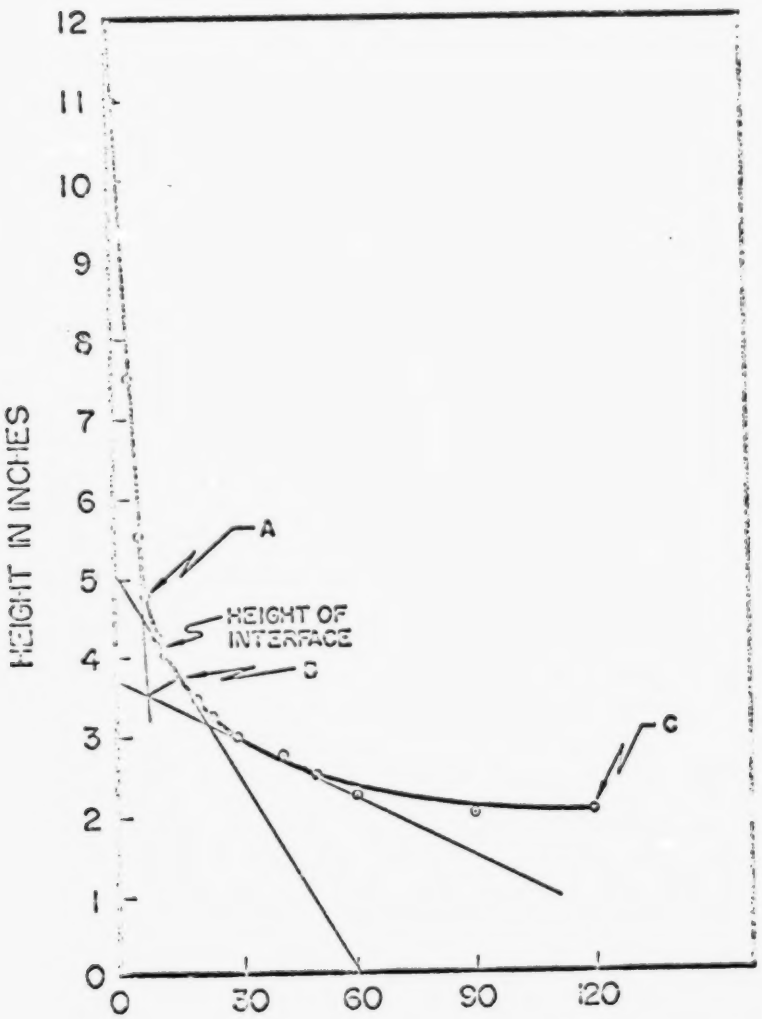



FIGURE A-4
TYPICAL SETTLING CURVE

## 6. Flotation Procedure

The flotation characteristics of the test mixture were estimated using the flotation apparatus shown in Figure A-5. The procedure was as follows:

1. Partially fill the calibrated cylinder with waste or flocculated sludge mixture and the pressure chamber with clarified effluent or water.

2. Apply compressed air to the pressure chamber to attain the desired pressure.

3. Shake the air-liquid mixture in the pressure chamber for one minute and allow to stand for three minutes to attain saturation. Maintain the pressure on the chamber for this period.

4. Release a volume of pressurized effluent to the cylinder and mix with the waste or sludge. The volume to be released is computed from the desired recycle ratio. The velocity of release through the inlet nozzle should be of such a magnitude as not to shear the suspended solids in the feed mixture, but to maintain adequate mixing.

5. Measure the rise of the liquid-sludge interface with time.

6. After a detention time to twenty minutes, the clarified effluent is drawn off through a valve in the bottom of the cylinder.

7. Relate the effluent suspended solids and the float solids to the calculated air-solids ratio. When pressurized recycle is used, the air-solids ratio is computed:

$$\frac{A}{S_a} = \frac{1.3 s_a R(P - 1)}{QS_a}$$

where:

$s_a$ = air saturation, cubic cm/liter

R = pressurized volume, liters

P = absolute pressure, atm

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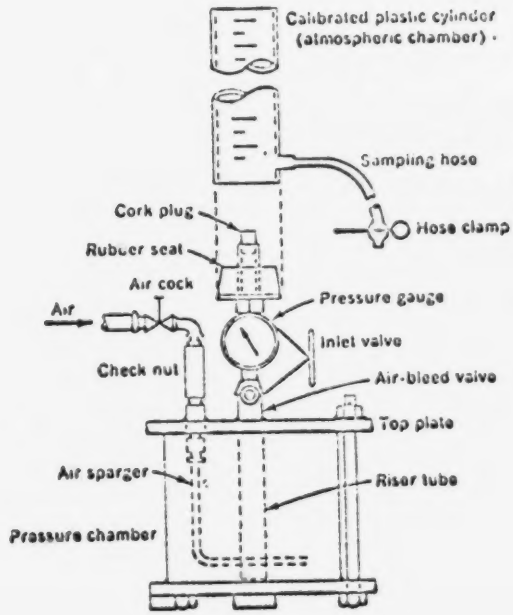


SCHEMATIC OF FLOTATION APPARATUS

FIGURE A-5

$Q$ = waste flow, liters

$S_a$ = influent suspended solids, mg/liter

Note: the foregoing relationship was modified in the report in order to relate the effluent oil concentration to the air to oil ratio.

## 7. Standard Jar Test Procedure

1. Using 200 ml of sample on a magnetic stirrer, add coaqulant in small increments at a pH of 7.0. After each addition, provide a one minute rapid mix followed by a three minute slow mix. Continue addition until a visible floc is formed.

2. Using this dosage, place 1,000 ml of sample in each of six beakers.

3. Adjust the pH to pH 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0 with standard alkali (see not below).

4. Rapid mix each 1,000 ml sample for three minutes; follow this with twelve minute flocculation at slow speed.

5. Measure the effluent concentration of each settled sample.

6. Plot the percent removal of characteristic vs. pH, and select the optimum pH.

7. Using this pH, repeat steps (2), (4), and (5), varying the coagulant dosage.

8. Plot the percent removal versus the coagulant dosage and select the optimum dosage.

9. If a polyelectrolyte is used, repeat the procedure adding polyelectrolyte toward the end of the rapid mix.

Note: Because this study was designed to simulate actual plant conditions, the pH was not varied. The chemicals were added to mixture at a pH = 7.0. Steps 1, 2, and 3 were not followed in this study.

## APPENDIX
## REFERENCES


Beerthuses and Kappler, "Gas Chromatographic Analysis of Higher Fatty Acid up to and Including Caustic Acid", Nature, London, 179, 1957, 731.

Hruinah and Polo, "Separation of $C_2$-$C_{18}$ Free Fatty Acids in Dairy Products by Dual Column P.T.G.C.," Journal of Gas Chromatography, June, 1967.

Maher, "Semi-Quantative Analysis of HydroCarbon Mixtures by Gas Chromatography Without Complete Separation of Components", Journal of Gas Chromatography, October, 1965 p. 335.

McPherson, Sawicki, and Fox, "Characterization and Estimation of n-Alkanes in Airborne Particulates", Jouranl of Gas Chromatography, April, 1966, p. 156.

Byars and Jordan, "An Efficient Packed Column for Free Fatty Acids", Journal of Gas Chromatography, September, 1964, p. 305.

Albert, G.C., "Determination of $C_5$-$C_{11}$ in Paraffins and Hydro Carbon Types of Gasoline", Analytical Chemistry, Volume 35, No. 12, November, 1963, p. 1918.

LePlat, P., "Application of Pyrolysis-Gas Chromatography to Study of Non-Volatile Petroleum Fraction", Vol. 5, No. 3, March, 1967, p. 128-35.

Girand, A., Bestorrzeff, M.A., "Characterization of High Molecular Weight Sulfur Compounds in Petroleum by Pyrolysis and Gas Chromatography, Journal of Gas Chromatography, Vol. 5, No. 9. September, 1967, p. 464-70.

Lively, L. Rosen, A.O., Mashni, C.I., "Identification of Petroleum Products in Water", Purdue University Engineering Ext. Ser. 1158, 1965, p. 657-63.

Farley, R.,Valentine, F.H.H., "Coagulation as Means of Separating Oil From Effluents", American Institute of Chemical Engineers, Advances in Separation Techniques Seminar, Paper #14 London, June 13-17, 1965, p. 36-45.

Martin, R.L., Winters, J.E., "Composition of Crude Oils by Gas Chromatography - Geological Significance of Hydro Carbon Distribution", World Petroleum Congress, 6th, - Composition, Analysis and Testing, Proceedings, Section 5, 1963, p. 231-60.

Dalbke, R.G., Lenny, A.M., Baumert, H., "Problems of Detecting and Controlling Fats, Oils and Greases at Their Source", Lubrication Engineering, Volume 21, No. 10, October, 1965, p. 433-38.

Davies, D.S., Kaplan, R.A., "Removal of Refractory Organics from Wastwater with Powered Activated Carbon", Journal of Water Pollution Control Federation, Vol. 38, No. 3, March, 1966, p. 442-50.

Maehler and Greenberg, "Identification of Petroleum Industry Wastes in Ground Waters", Journal Water Pollution Control Federation, Vol. 34, No. 12, December, 1962, p. 1262-7.

Hoah, R.D., "Recovery and Identification of Organics in Water", Air and Water Pollution, Volume 6, November-December, 1962, p. 521-38.

Cochran, L.G., and Bess, F.D., "Waste Monitoring by Gas Chromatography", Journal Water Pollution Control Federation, Vol. 38, No. 12, December, 1966.

Hoah, R.D., Caruso, S.C., Bramer, H.C., "Tracing Organic Compounds in Surface Streams", Air and Water Pollution, Volume 10, No. 1, January, 1966, p. 41-8.

Dalbke, R.G., Tenney, A.M., and Baument, H., "Problems in Detecting and Controlling Oils, Fats, and Greases at Their Source", Lubrication Engineering, Volume 21, No. 10, October, 1965, p. 433-8.

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*Bench Scale studies, *Spent crankease oil, *Vegetable oil, *Crude oil, *Refinery waste oil, *Load tolerance, *Continuous, *Shock

27 Abstract

Small scale continuous activated sludge systems were exposed to a variety of oily compounds at several loading levels and performance obaerved. Batch studies to determine biodegradability and the effect of emulsification and temperature on the rate of biological reaction were also conducted.

Oils introduced into an activated sludge system are absorbed on the floc and slowly degrade. If the loading rate is higher than the degradation rate and the rate of wastage, the oil accumulates on the sludge. This accumulation causes a loss of density and a loss of acceptable settling characteristics. The biological system fails due to the loss of sludge but the ability of the microbial system to remove other substrates is not inhibited.

The continuous feed level of oils to activated sludge should not exceed 0.10 pounds per day per pound of sludge under aeration. Shock loads should not exceed 5% of the weight of the sludge under aeration.

The study also considered physical separation of oils before biological treatment, and various chemical methods of separating complex emulsions.

Abstractor Edward L. Dulaney | Institution Water Quality Research, EPA

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